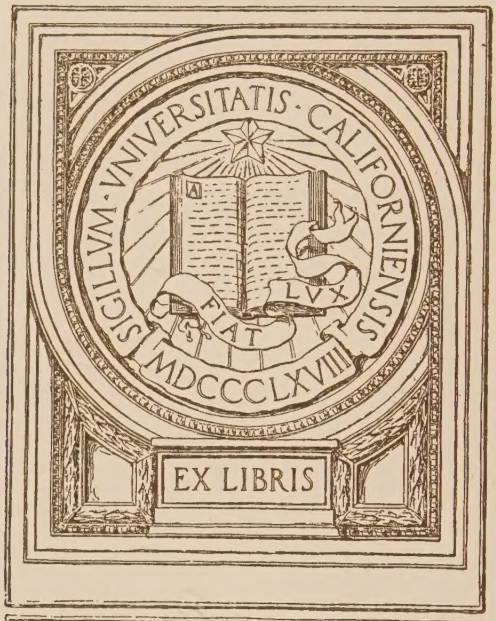

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PROTECTIVE METALLIC COATINGS

BY

HENRY S. RAWDON

SENIOR SCIENTIST (METALLURGY)

UNITED STATES BUREAU OF STANDARDS

American Chemical Society
Monograph Series

BOOK DEPARTMENT

The CHEMICAL CATALOG COMPANY, *Inc.*

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

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The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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Preface.

The subject of protective metallic coatings is intimately related to the much broader one of the corrosion of metals. Protective coatings are properly to be considered as one of the important methods of corrosion mitigation, and it is principally from this standpoint that the subject has been treated here, although it is recognized that the term "protective metallic coating" may be used in a broader sense and such subjects as the case hardening of steel be included if desired. The practical side of the subject of coatings far outweighs its more theoretical aspects. Indeed, so varied and unrelated in nature are the different methods used for the production of metallic coatings that any critical discussion of the fundamentals of the different methods would soon lead to very wide digression from the subject in hand.

In preparing this book, the author has attempted, first of all, to give a discussion of those characteristics and properties of the various types of metallic coatings which determine the usefulness of such coatings as well as their limitations, with the hope that the book might be of some value and interest to the non-technical reader as well as to the specialist in metallurgy or chemistry. For this reason, certain portions of the discussion may appear to the specialist as somewhat elementary. The essentials of the various coating processes have been given, since the characteristics of any coating and consequently its usefulness are often determined in very large measure by the process by which it was produced. No attempt, however, has been made to include the working details of the various methods or to make the book serve in any way as a shop manual on coating processes.

Since it is for the protection of iron and steel against corrosion that protective coatings are most generally used, this phase of the subject has been referred to repeatedly throughout the book. Nearly all of the investigative work on the testing of metallic coatings has been devoted to zinc coatings since this class is used so extensively and is so important from the industrial standpoint. The discussion of this phase of the subject has, of necessity, been limited in like manner.

Although a good deal has been written on the different phases of

the subject of coatings, the number of articles which are really worthwhile is surprisingly small. The author has drawn freely upon his own experience at the institution with which he is connected to supplement the information obtained from a review of the technical literature.

It is a pleasure to acknowledge the help received from many of the author's associates at the Bureau of Standards and especially from a number of friends in the reading and criticism of certain portions of the book. In particular, the criticisms of Mr. E. S. Taylerson, Metallurgical Engineer, American Sheet and Tin Plate Company, on the chapters on zinc and tin coatings; of Mr. W. H. Finkeldey, Assistant Director, Research Laboratory of The New Jersey Zinc Company, on zinc coatings; and of Mr. E. F. Kohman, Chemist, Research Laboratory of the National Canners' Association on tin coatings have been most helpful and have been incorporated into the text.

H. S. Rawdon.

September 12, 1927.

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PROTECTIVE METALLIC COATINGS

Chapter 1.

Introduction.

To some, the term "coated metal" suggests an inferior, or at least a second-class, product. This idea originated in the early use made of gold and silver coatings to give the outward appearance of the solid metal, a practice dating from early Egyptian times and also known to the metal workers of the early American "civilizations" such as that in Peru. The difference in the manner in which sterling silver and silver-plated tableware are usually regarded today by housewives is typical of this attitude toward coated metals. Present-day commercial metal-coated materials are, for the most part, in a very different class, however, and the fact that a material is coated is in many cases to be regarded as a mark of relative superiority rather than the reverse.

In by far the greater number of cases, coatings on metals are used as a protection against atmospheric corrosive attack of the underlying or "base metal." Corrosion by sulfur and sulfur compounds is another problem of considerable commercial importance especially in connection with petroleum refining and related industries. Protection against oxygen and sulfur attack constitutes the main reason for the use of metallic coatings. Iron (steel) is the metal used in the largest quantities in engineering undertakings and, without doubt, will continue so to be used. Its protection from corrosion, therefore, is of the greatest economic importance.

Corrosion of any metal usually necessitates the dissolving of the metal. The metal exists in the final corrosion product in a higher state of oxidation than it did in the uncorroded or metallic state. To protect a metal from atmospheric corrosion it is essential and adequate, then, that access of moisture (liquid water) to the surface of the metal be prevented. A simple way of doing this is to oil the surface. Instances of this practice about the household are so common and familiar that mention of them seems unnecessary.

The industrial applications of this method of allaying the corrosion

of iron and steel products by means of oil or grease coatings, generally known as "slushing compounds," are many and varied. An important example is that of the machinist who coats his machine and tools with slushing oil prior to "closing down" for any length of time. The protection from corrosion of the finished surfaces on lathes and similar machines as well as on a great variety of machined and polished steel articles during shipment is also ensured in the same way. A good slushing compound as a rule gives a high degree of protection from corrosion as long as the grease film remains intact. It is, of course, necessary that any such slushing compound be chemically inactive toward the metal to be coated, also that the surface of the metal be free from traces of acids or such substances as chlorides which would promote corrosion, as it has been well established that corrosion will take place under oil films if the metal has not been cleaned sufficiently prior to oiling it. The "life" which may be expected of any coating of grease varies, of course, with the amount of the grease used and also with its nature. Moisture will permeate a thin grease coating as the character of the coating alters because of oxidation or other changes. Very highly polished surfaces kept coated with a slushing compound sometimes show evidence of microscopic etching after storage. On ordinary articles, however, an attack of this nature would be entirely negligible. From the results of a recent investigation, Jakeman [A 21][1] concluded that a slushing compound having a lanolin base is preferable to those of other types for very severe service, especially if rather high temperatures are involved.

Despite the fact that grease coatings of this kind are intended primarily for use on metals in storage rather than in service, some of them have been used with considerable success, although to a very limited extent, for the protection of metals while in active service, such as airplane parts. Obviously, the harder compounds are the most suitable for such a use. Furthermore, the practice of greasing or oiling certain types of coatings which in themselves give very little protection to the metal which they cover is not at all uncommon. By this means, the protection afforded by such coatings can be increased many fold (*See* Chapter 12).

Any metallic or similar coating protects the metal to which it is applied against atmospheric corrosion in exactly the same way as does a coating of grease, paint or enamel, that is, it excludes air and moisture. It is essential to keep moisture out since the fact is well established that metals do not corrode in dry air. It would seem to be a valid conclusion,

[1] Letters and numbers in brackets refer to references quoted in the Bibliography beginning on page 237.

therefore, that the more resistant to corrosive and abrasive influences a metal coating is, either because of its intrinsic properties or because of any protective film which may form on it as a result of initial corrosion, the longer will be the life of the coated article as a whole. This conclusion is only partly true, however. As long as the coating is intact at all points, so that the base metal is everywhere completely covered, the conclusion that the corrosion resistance of the coating determines the life of the coated article is valid. This is not so, however, if the coating is not impervious at all points, a condition which may obtain either because of the natural wear to which the coating may be subjected, or on account of defects initially present in the coating.

Some metallic coatings prevent the corrosion by ordinary corrosive agencies of the base metal which they cover, even though the coating is not impervious to the passage of air and moisture through it. Such a protective action is dependent upon a difference in the "solution pressure" of the metal of the coating as compared with that of the base metal. Metals differ decidedly in their solution pressure or tendency to dissolve, that is, to pass from the metallic condition to the ionic state when wet with an electrolyte. When two unlike metals in intimate contact with one another are exposed simultaneously to corrosive attack by a solution, the one having the greater solution pressure, corrodes, that is, dissolves, and by so doing prevents in very large measure any corrosive attack of the other. The greater the difference in the solution pressures of the two metals, the greater the degree of protection afforded by one metal to the other, although practical considerations such as the relative size of the specimens play an important part. It is to be noted, also, that the rate at which the first metal corrodes is greater while it is in contact with the second metal than when it is immersed alone in a solution. If a metal used as a coating has a greater solution pressure than has the base metal which it covers, then when as a result of a defect in the coating both are exposed simultaneously to a corroding reagent, the coating dissolves slightly and the base metal remains untouched until the attack has been continued long enough so that a good deal of the coating has been removed.

The solution pressure of a metal cannot be measured directly but must be calculated from other data. Such numerical values serve mainly to place the metals in the order of their relative solution pressures. The same information is given by the familiar "electromotive series" of metals, and for all practical purposes, so far as corrosion of metals is concerned, this series serves for the purpose of discussion just as well as the calculated values of the solution pressures. This series, taken from Evans [A 15], is given in Table 1. The order in which the metals

stand in the series corresponds, in general, to the order of increasing solution pressure of the metals. The calculated value for the solution pressure of a "reactive" metal such as magnesium is an excessively large number, whereas for a "noble" metal such as platinum it is exceedingly small. In any discussion of the relative corrodibilities of metals as based upon the electrochemical series, it should be stated at the outset that complete agreement has, as yet, not been reached concerning the exact order in which some of the metals should be placed. The "single potential" of a metal, as given in such a table, represents a state of equilibrium in a given solution of a stated degree of ionization. Such a condition is not reproduced in actual corrosion conditions. Not infrequently the tendency toward corrosion, or at least the rate at which a metal corrodes, decreases very noticeably as corrosion proceeds. The electrochemical series, however, despite its limitations forms the most convenient basis of discussion of the relative corrodibility of the various metals which we have.

The data given in Table 1 summarize concisely the behavior of the various metals when wet with a solution of the same metal, in other words, the condition necessary for equilibrium between the atoms of a metal and ions of the same metal. When a metal is immersed in a solution of the same metal, there is a tendency, the intensity of which

TABLE 1.—ELECTRODE POTENTIALS OF METALS.

Difference of potential at the interface between a metal and its solution of normal ionic concentration in which it is immersed [A 15, N 16].

Metal	Ion	Difference in Potential
		Volt
Gold (approx.)	Au''	+ 0.985
Platinum	Pt''''	+ 0.86(?)
Silver	Ag'	+ 0.7987
Mercury	$(Hg')_2$	+ 0.7928
Copper	Cu''	+ 0.3469
Hydrogen	H'	0.000
Lead	Pb''	— 0.132
Tin	Sn''	— 0.146
Nickel	Ni''	— 0.20
Cobalt	Co''	— 0.23
Iron[1]	Fe''	— 0.34
Cadmium	Cd''	— 0.420
Chromium	Cr'''	— 0.47
Zinc	Zn''	— 0.770
Aluminum	Al'''	— 1.337
Magnesium (approx.)	Mg''	— 1.8
Sodium	Na'	— 2.715
Potassium	K'	— 2.925

[1] Complete agreement concerning the position of all the metals has not yet been reached. Some authorities place cadmium above iron in the list. There is also uncertainty as to the relative position of some of the other metals, for example tin and lead.

varies with different metals, for more atoms of the metal to enter the solution (solution pressure), while there is an equal tendency in the opposite direction within the solution, that is, for metal to be deposited from the solution upon the metal surface. By suitable means, such as are described in any text book on electrochemistry, the difference of electrical potential at the interface between the metal and the solution in which it is immersed can be measured. The numerical values of this potential difference are the numbers which are given in Table 1. Consider the case of copper: equilibrium at the surface of a specimen of copper immersed in a copper solution of the concentration stated can exist only when there is a potential difference of $+0.3469$ volt. If by any means the potential difference is increased somewhat, for example, by using an external source of electromotive force, more copper atoms will pass from the surface of the specimen (anode) into the solution as copper ions. On the other hand, if this potential difference is depressed below the equilibrium value, copper ions will leave the solution and deposit as atoms on the metal surface (cathode). This is illustrated in the case of two copper strips immersed in a copper solution and connected outside of the solution by a wire. Since the potentials of each copper specimen with respect to the solution is the same, nothing happens. However, if the specimens, while immersed, are connected to a source of electromotive force, the potential of one copper specimen (anode) with respect to the adjacent solution will be increased above the equilibrium value and the potential of the other (cathode) will be depressed, and as the "current is passed through the cell" dissolving of copper (corrosion) occurs at one pole and deposition at the other.

Similar conditions obtain when two dissimilar metals, that is, metals having different solution pressures, each immersed in the corresponding metal solution, are electrically connected—for example, copper immersed in a copper solution and zinc immersed in a zinc solution, the two metals being connected outside of the solution by a wire and the two solutions brought into contact with one another, with a minimum amount of intermingling. Since the potentials of the two metals with respect to the corresponding solution are quite different, when electrical contact is established between them the potential of each will change as the current flows through the circuit. At the zinc end of the combination, the potential difference at the interface between metal and solution will be increased above the equilibrium value (made less negative) and zinc atoms will enter the solution and form more ions. At the copper end the opposite condition will obtain. The potential difference at the interface between copper and solution will be lowered (made less positive) by the contact with the zinc, hence copper ions can leave the

copper solution and deposit in metallic form on the copper specimen. The passage of a continuous current of electricity through the wire is made possible by these conditions. A primary battery as illustrated above may be regarded as a device which takes advantage of the difference in solution pressure of different metals for producing electrical energy.

The values given in Table 1 are strictly applicable only to the case of metals immersed in solutions of the same metals. The underlying principle, however, has a more general application. Suppose two dissimilar metals in intimate contact, such as a small plate of iron in which a plug of zinc has been inserted, are immersed in a solution, for example, of sodium chloride. The potential difference at the interface between each of two metals and the solution will not be the same. The values will not be those of Table 1 for these two particular metals, but for a good many electrolytes the potential differences between each of the two metals and a given solution will stand in the same relation to each other as in Table 1. The conditions then are essentially the same as those of the case of copper and zinc just described. Atoms of the more reactive of the two metals, zinc in this case, pass into the ionic state, and ions of another character leave the solution and deposit upon the surface of the less reactive metal, iron; a current passes through the conductor, which in this case is the composite specimen itself. The zinc plug functions as the anode, the iron as the cathode of a cell. Since no ions of iron are being added to the solution, no "corrosion" of the iron is taking place. The zinc, on the other hand, does corrode actively. We generally speak of the iron as being "protected from corrosion" by the presence of the zinc, and the fact that the protection is afforded only by the gradual corrosion of the protecting metal, zinc, is not always fully appreciated.

The difference in the electrochemical properties of the common metals, zinc, cadmium, lead, copper, nickel, aluminum, and tin, with respect to iron is illustrated in Figure 1. Small plugs of the different metals shown were inserted in mild steel plate, one in each specimen. The surface was then planed smooth and polished with 00 Hubert emery paper. After cleaning, the specimens were immersed in 0.5 *N* sodium chloride solution in an enameled tank and allowed to stand. The corrosion effect after 18 hours is shown in Figure 1. The protective action of the zinc and of the cadmium toward the iron is very evident, that of the aluminum is not quite so plain. This may be accounted for, however, by the well-known tendency of this metal to become inactive by the formation of a protective film, presumably oxide or hydroxide, as a result of the chemical action occurring. The results shown in Figure 2,

Fig. 1. Electrochemical corrosion of steel when in contact with another metal [H 11]

A plug, one-half inch in diameter, of the metal indicated was inserted in a mild steel plate which was then immersed in O.5*N* sodium chloride solution for 18 hours. Note the complete protection afforded the steel by the zinc and the cadmium plugs and the partial protection by the aluminum. In all the other cases the steel surface was covered with a heavy deposit of "rust." Note how the surface of the cadmium and zinc plugs was etched by the anodic corrosion which occurred.

which were obtained with each of the four metals, zinc, cadmium, chromium, and copper, when in contact with electrolytic iron and kept wet with sodium chloride solution, confirm those of Figure 1.

The examination of the face of the metal insets in the above experi-

ment after immersion in the sodium chloride solution clearly showed the source of the protection afforded the steel specimen in those cases in which corrosion of the iron was inhibited. The faces of the cadmium and the zinc plugs were found to be deeply etched as a result of the chemical action so that the crystalline structure was clearly revealed. These metals had been subjected to anodic corrosion. This was not

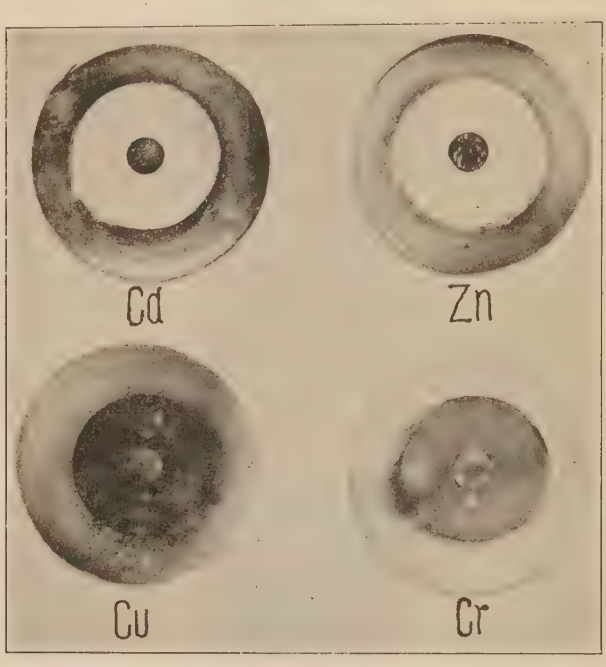

FIG. 2. Electrochemical protection of pure iron when in contact with another metal [H 11].

Compare with Fig. 1; the corrosion conditions are similar. The inner circle is the metal plug inserted in the disc of iron, 1½ inches in diameter. The outer ring is the dish containing the solution in which the specimen was immersed. The iron discs with zinc and cadmium inserts were protected against corrosive attack but not by copper or by chromium.

so evident with the aluminum, for the reason already given. No etching effect was noted in any of the metal plugs in those specimens in which the iron corroded, nor should any be expected. There can be no doubt, whatever, of the anodic nature of both zinc and cadmium with respect to iron when in intimate contact with it and immersed in sodium chloride solution. It is to the preferential attack of these metals by the solution that the protection of the iron is to be attributed. Likewise, although it is not evident from Figures 1 and 2, in those cases in which the iron was severely corroded the intimate contact with a metal more noble than

iron, as indicated in Table 1, serves to hasten the corrosive attack of the iron or, in other words, the iron in such a case may be thought of as functioning as the anode and protecting the inserted metal, such as nickel or lead, from corrosion by the sodium chloride solution.

The action which takes place when two metals intimately connected are wet with an electrolyte of some kind is fundamentally dependent upon the nature of the two metals and not upon the form or manner of their union. Obviously, if the more reactive metal were spread out as a layer over the surface of the other one with the underlying metal exposed only here and there through perforations of the coating, the action would still be of the same general nature as illustrated above. By the preferential dissolving of the coating metal, the base metal, even though not perfectly covered, would be protected against corrosive attack for a considerable length of time. Not until the coating metal had been corroded away very appreciably would the underlying metal show corrosion. On the other hand, if the more noble metal were spread over the more reactive one as a coating, at any perforation of the coating the attack of the underlying metal would be accentuated. On account of the relatively large area which would serve as a cathode in contrast to the small anodic areas (perforations) the attack of the latter would be greatly accelerated so that severe pitting would ensue.

The example above, of an iron disc containing a zinc insert immersed in a sodium chloride solution, of course does not closely parallel in all respects the ordinary service conditions for coated metal in which the coating is more reactive than the base. In the first place, for a zinc-coated metal, for example, so long as the zinc coating remained intact throughout, any corrosive attack of the coated article as a whole would be the same as that of a piece of zinc, and the electrochemical protection of the base by the zinc would not manifest itself. Secondly, the actual corrosive conditions to which such coatings are exposed are in practically all cases very much less severe than immersion in a sodium chloride solution; hence, even after the base metal had been exposed, the two conditions of corrosion would still not be analogous in all respects. In particular, in the case of the immersed specimen the protective action of the zinc would be expected to extend over a very considerably larger area than would be the case in a similar specimen exposed only to atmospheric conditions.

Figure 3 which summarizes data obtained by Bauer [A 5] presents in graphical form information similar to that depicted by Figures 1 and 2.

According to the values of the normal electrode potentials summarized in Table 1, the common metals, zinc, cadmium, aluminum and

chromium, when used as coatings on iron or steel, might be expected ordinarily to exert a protective influence and inhibit the corrosion of the base metal when the coating and base are wet simultaneously by an electrolyte. Experience shows, however, that chromium does not give to iron and steel the protection expected of it from its position in the

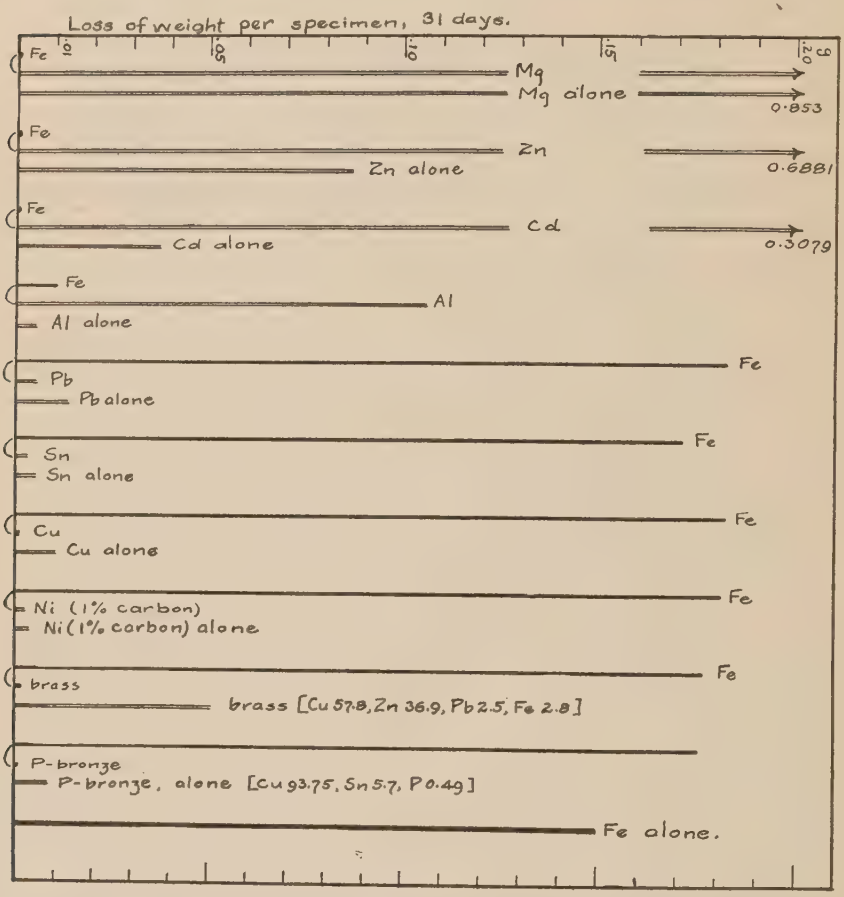

FIG. 3. Relative rate of the corrosive attack of one per cent sodium chloride solution on iron and other metals when in intimate contact and also when immersed singly in the solution [A 5].

series although it is by no means certain that this position is the correct one. This behavior may be because the metal does not remain in the active state but becomes passive perhaps by the formation of a protective surface film. In such a case it would behave as a neutral coating which, while not inhibiting the corrosion of the iron by its electro-

chemical behavior, also would not hasten the corrosive attack. Likewise, aluminum cannot be depended upon to give to iron and steel as good electrochemical protection from corrosion as might be predicted from a knowledge of its position in the electrochemical series, although it behaves very much better than chromium in this respect. The tendency of aluminum and magnesium to form an adherent continuous filmlike coating as a result of oxidation, which shields the metal to a very appreciable extent against further oxidation so long as the film is intact, may often modify considerably the electrochemical behavior of such a metal when used as a coating. This tendency may also be observed with other metals under certain conditions of usage, and any prediction based alone on the electrochemical series as to the performance in service of a metallic coating may be subject to some qualification and limitation.

The other common metals, copper, nickel, lead, and tin, in the form of coatings on iron or steel can protect the base metal in a mechanical way only, by excluding the corrosive influences in exactly the same way that a paint or enamel coating does.

Chapter 2.

Coating Methods Depending Upon the Alloying of Coating and Base.

Immersion in Molten Metal—"Hot-dipping."

The oldest and most familiar of the commercial processes used for applying metallic coatings to other metals is that commonly known as "hot-dipping." Essentially this process consists in immersing bodily the article to be coated in a bath of molten metal for a short time, usually very little, if anything, additional being done to change the properties of the metal coating which adheres to the surface upon removal of the article from the molten metal bath.

Principles.

For the successful coating of one metal with another by means of the hot-dipping process, it is necessary that the two metals alloy with each other, at least to some extent. A *clean* glass rod when dipped into water and withdrawn is found to be covered by an adhering film of moisture, the force of surface tension serving to make this film uniform over the surface which was wetted. The production of a metal coating by immersion in a bath of molten metal is not strictly analogous to this simple illustration, however, but is more like the case of the immersion of a crystal of rock salt in water. The film which covers the surface in this case is not one of pure water, but contains an appreciable amount of the salt in solution. It is decidedly easier also in this case, because of the tendency of the substance to dissolve, to produce a uniform coating film over the surface of the immersed crystal. The dissolving of the small amount of salt by the enveloping film of water is strictly analogous to the alloying action which occurs during the hot-dipping coating process and which makes this process a successful one for the coating of metals. The alloying of iron with the molten zinc or tin is generally regarded by the men engaged in the zinc or tin coating industry as a more or less unavoidable nuisance incidental to the process. It is not generally recognized that, fundamentally, success in this process is attained almost entirely because of this behavior of the two metals.

In most cases of the commercial coating of metals by hot-dipping, the coating metal, zinc, tin, or aluminum, for example, alloys very readily with the "base metal", that is, the metal to be coated, for example, iron. In case the coating and base metals do not alloy directly, the same end may often be accomplished by the use of a small amount of a metal which does alloy with both of the others. This is usually done by making a suitable addition to the molten metal bath, though the same result may be attained if the "addition" is made as a surface film on the base metal before immersion in the molten metal. As will be explained later, although there is no mutual alloying whatsoever between the metals lead and iron, lead coatings on iron and steel are often secured by this means.

Although hot-dipping is essentially a method depending upon surface alloying, it should not be inferred that no coating whatever can be obtained if alloying between coating and base is lacking. Just as in the case of the clean glass rod when immersed in water a film is produced over the surface, so also, if a *clean* metal surface, for example, iron, is brought in contact with a clean molten metal with which it does not alloy, lead for instance, a continuous coating film of the latter can often be made to cover the surface. The difficulties in producing such a continuous coating under these conditions are so great, however, as to render the process impracticable. Much of the difficulty arises as a result of the tendency of the coating during its solidification to coalesce more or less into globules thus giving rise to breaks in the coating. This tendency is counteracted by the alloying action between the coating metal with the base.

The necessity for some alloying action between coating and base metals, in the hot-dipping coating process, is twofold, therefore, although the second may perhaps be considered as a corollary of the other. First, slight alloying of the two insures a complete initial "wetting" of the surface of the base metal and therefore a uniform spreading of the molten metal over the surface; and second, as a result of this, the adhering film of metal solidifies without exhibiting any pronounced tendency to draw away from the base.

General Nature of Hot-dipped Coatings.

In no case is a metal coating which is produced by the hot-dipping process a simple film of the pure coating metal. As an unavoidable consequence of the necessary mutual alloying action, the coating must always be contaminated more or less with traces of the base metal, and its structure and properties must be somewhat different from those of a similar layer of the pure metal.

In structure a hot-dipped coating always shows evidence of at least two more or less distinct layers, the inner one being usually referred to as the "alloy layer". The metals used for coatings in the hot-dipping process are decidedly different in most of their properties from the base metals which are to be coated. The alloys formed by the union of unlike metals are usually not of a simple type such as simple solid solutions or plain eutectic series but of the more complex types in which intermetallic compounds occur. The inner or alloy layer of the coating of a hot-dipped coating practically always is made up in large measure of an intermetallic compound of the two constituent metals. Consequently this part of the coating is harder and more brittle than the outer layer which consists largely of the plain coating metal.

When a metal of high melting point, such as iron, is immersed in a molten metal of low melting point with which it alloys, such as zinc or tin, traces of it dissolve in the melted metal in the same way that salt dissolves in water. At the same time the molten metal combines with and diffuses to some extent into the solid metal, giving rise to a definite alloy layer. If the process is allowed to continue the diffusion may extend inward far enough so that a second layer forms which is different from the first in its composition and properties. It is a singular fact that the alloy layers formed in this manner do not gradually merge, one into the other, but each is of a quite definite composition, and the change from one layer to the next is a decidedly abrupt one. When the immersed specimen with its outer alloyed surface is removed from the metal bath, it carries with it a surface layer of molten metal which by solidifying forms the outer layer of the final coating.

The relative thickness of the alloy layer in any hot-dipped metal coating varies with the kind of coating. For example, in a tin coating on iron this layer is very thin, whereas in a zinc coating on iron the alloy layer may under some conditions constitute the greater part of the coating. Since the amount of alloying in any case depends also upon the time and the temperature both of these factors must be carefully regulated in practice. Prolonged immersion in the molten metal results in the formation of a thick alloy layer which renders the coating so brittle that for many purposes it may be useless.

Practical Aspects of the Hot-dipping Process.

In the simplest applications of the hot-dipping process, very little equipment besides handling tools and a container for the molten metal is required. For the coating of the vast quantities of sheet and wire, however, which is done almost exclusively by this process, very elaborate mechanical devices have been developed. These are referred to briefly in

later chapters. Hot-dipped coatings are nearly always relatively thick as compared with other types of coatings. In many respects, however, the hot-dipping process is somewhat wasteful of metal since there is no way of controlling accurately the amount of coating metal used and its distribution over the surface. In the case of materials of regular shape, such as sheet and wire, the uniformity of the coating can be regulated mechanically fairly well and the excess metal wiped off. With small pieces—nails, bolts, screws, and the like—a centrifuge is used to advantage in regulating the amount of coating metal put on, but for the great majority of pieces there is no simple and sure method for regulating both the amount of metal used and its distribution as a coating over the surface.

The hot-dipping process is a commercial success only with metals of relatively low melting point. For zinc and tin coatings and for some of the lead alloy coatings, its use forms the basis of one of the leading industries. Of the other metals of lower melting point, aluminum (m. p. 658.7° C., 1218° F.) is the only one which is used, and this only to a very limited extent. The production of cadmium coatings (m. p. 320.9° C., 609° F.) by hot dipping has not been seriously considered on account of the limited production of this metal. The difficulties attending the handling of molten metals of high melting points, such as copper, nickel, or cobalt, in the large amounts necessary for the process have not encouraged experiments in the application of coatings of these metals by this process. The detrimental effect of the high temperature involved, if such coating metals were used, upon the properties of the metals to be coated, is also a factor which is not encouraging.

Extension of the Hot-dipping Process.

If, instead of totally immersing the article to be coated in molten metal, a small amount of the coating metal is melted on the surface to be covered and then rubbed thoroughly over the surface, a coating can be produced which, in its essential respects, is the same as a hot-dipped coating. The tinning of copper sheets and containers is usually done in this manner. A slightly modified process consists in applying the coating metal as a powder mixed into the form of a paste with a substance which serves the double purpose of binder and flux. When heated, the paste melts and under the influence of the flux spreads as a thin film over the surface. The process is of very limited commercial application or importance, however. Its use has been proposed for the metals of low melting point, lead, tin, and zinc, and also for the production of copper coatings. In the latter case, an oxide of the metal

which is reduced upon heating in a reducing atmosphere may be used. The method appears to be most useful for the coating of local bare spots in otherwise sound coatings.

Cementation.

Cementation is another means of surface alloying and finds numerous metallurgical applications which depend upon the modification of the surface of a metal, the most familiar of which is the important process of "case hardening" of steel. By heating a soft, ductile (low carbon) steel at a suitable temperature while it is surrounded by a carbonaceous packing material, the metal at the surface is converted to a considerable depth into a high-carbon steel by combining chemically with carbon which diffuses into it in the form of a gaseous compound. Subsequently, by suitable heat treatment, this modified surface layer can be made glass-hard and of high "wear-resistance," whereas the interior is only slightly changed and remains relatively strong and tough. The principle of cementation is also utilized in the production of surface layers on metals which serve as protective coatings against corrosion and other forms of deterioration.

Principles.

The characteristic feature of cementation, like that of hot-dipping, is a very appreciable alloying action of the surface layer of the treated metal. Unlike hot-dipping, it does not necessitate the use of a molten metal but consists in heating the metal while surrounded by another metal or non-metal, generally in powdered form, to a temperature somewhat below the melting point of the more fusible of the two.

The process is of rather wide metallurgical application and the practice of ancient metallurgists of converting copper to brass by heating in certain "favorable earths" is often cited as an example. The "favorable earths", of course, contained some zinc minerals. Roberts-Austen [B 152], in his discussion of the diffusion of metals in the solid state, has well summarized the historical side of the cementation process and shown its great antiquity. He describes cementation as "really a slow creeping of one metal into another" and considers that the process "must be closely connected with the evaporation of solid metals and alloys at temperatures far below their melting points".

The observations made by Faraday and Stodart in 1820 on the alloying of platinum with iron at a relatively low temperature are referred to by Roberts-Austen as perhaps the most striking fact in the more modern history of the subject. Spring carried out experiments in 1882 showing that alloys may be formed at ordinary temperatures by com-

pression of the constituent metals, while Lehmann in 1885 suggested and Hallock in 1888 demonstrated that alloying takes place without pressure if the clean metals are in contact and are heated to the fusion temperature of the alloy which forms. Spring in 1894 showed that very considerable alloying by cementation will result if the ends of two carefully surfaced cylinders are pressed together and held at a temperature varying from 100° to 400° C. according to the nature of the alloys formed [B 152].

Considerable difference of opinion has been expressed, by recent writers on the subject of the production of coatings by cementation, concerning the "mechanism" of the process. By some [B 162, B 172] it is held that *intimate* contact at the cementation temperature between the particles of the cementing metal and the base metal is sufficient. Others [B 157, B 174] contend that the vapor pressure of the cementing metal at the temperature used, although slight, is sufficient to account for the transfer of the metal onto the surface of base metal. Both of the factors undoubtedly contribute to the building up of the coating, as the process is carried out commercially. It is well known, in zinc cementation, that the intimate contact secured by "tumbling" the articles while being heated within the packing of zinc powder is necessary to secure uniform coatings. The volatilization of the cementing metal may aid in building up the deposit in microscopic crevices into which the particles of metal could not penetrate.

Character of the Coating.

A coating produced by cementation is simply a surface alloy layer of the base and coating metals. In most essential respects, it is comparable to the inner or alloy layer of a hot-dipped coating of the same metal. The coating metal, as such, does not enter into the structure of the coating except as particles may be mechanically entrained perhaps as a result of partial fusion resulting from too high an operating temperature.

It is characteristic of the process of cementation, at least for those metals which are capable of forming definite compounds with each other, that the alloy layer produced is not one in which the composition changes gradually from that of the "cementing" metal on the outside to that of the base metal on the inside. On the contrary, the coating is composed of sharply defined layers each of which is quite homogeneous, at least in its visible structure. Storey [B 173] has described the case of copper cemented with zinc dust which forms an excellent demonstration of the structure of such coatings, on account of the difference in color of the different layers which form. The outer silvery gray layer is much

higher in zinc than is the other one, which is a brilliant golden yellow, adjacent to the copper base. The relative thickness of the layers which make up the coating, and hence the average zinc content of the coating, is determined largely by the cementation temperature.

Alloy coatings are considerably harder and more brittle, as a rule, than those of the pure metal, and the chemical resistance is not the same as is that of the pure metal. In any comparison of the relative merits of coatings of the same metal made by different process, for example, zinc coatings made by cementation and by electroplating, it should be borne in mind that metallurgically the two are of entirely different natures. Strictly, they are comparable only to the extent that they are used for the same service.

Practical Applications.

The use of the cementation method for producing coatings is necessarily restricted to those metals which alloy readily with the base which is to be coated. Three successful applications of this principle to the production of protective coatings have been made. Special trade names have been applied to these methods; "sherardizing" for cementation by means of zinc powder, "calorizing" for cementation by aluminum powder, and "chromizing" for the similar production of a coating of chromium. While these processes are used almost exclusively in the production of coatings on iron and steel, their application to other metals is apparent. The utilization of the cementation principle in the steel industry for the production of a surface layer of a hard wear-resistant high-carbon steel on a relatively soft base will not be discussed in this book. Although such a layer can, in a sense, be considered as a "protective metallic layer", it does not fall within this category, according to the way this term is generally understood and is used in this book.

The cementation process, although particularly well adapted for small pieces, cannot very well be carried out on a small scale. The pieces are packed in the cementing metal powder in rather large containers which can be made fairly gas-tight and which can be rotated about one axis so as to tumble the cementing powder over the surfaces to be coated. The whole must be heated for several hours and this is most conveniently done by means of electric heating coils in the walls of the container. In some cases, as in calorizing, the process must be carried out in the absence of air, usually in an atmosphere of hydrogen.

The Mechanical Coating Method.

Although this method cannot be classified simply as a surface alloying method, alloying of the two metals is essential to its success. The

method depends upon the simultaneous rolling of two unlike metals in intimate contact with each other and is, from its nature, applicable only to rolled metal products. If a duplex ingot is made of two metals, that is, the central portion of one metal surrounded by a thick layer of the other, such as an iron or low-carbon steel center and copper covering, it is possible to roll the duplex ingot into the form of coated plate, bar or sheet; coated wire may also be drawn from a duplex billet. The finished product, in the example cited, has a coating of copper intimately alloyed to the steel base, the thickness of the coating being governed by the relative amounts of copper and steel in the ingot used and the amount of reduction received in working. Obviously the process is applicable only for those metals that do not differ radically in their rolling characteristics. The process has been used commercially for coating soft steel with copper, with nickel, and with copper-nickel alloys. The old process for making Sheffield plate depended on the simultaneous rolling of silver and a copper-rich alloy.

Chapter 3.

Electroplating.

Nearly all of the metals used commercially as protective coatings can be deposited as firmly adhering coatings electrolytically from aqueous solutions directly upon the surface to be covered. Aluminum is an outstanding exception. Copper, nickel, and zinc plating constitute very important industrial applications of the electrodeposition of metals while the plating of silver and gold marks the beginning of the electroplating industry. The successful plating of chromium on a commercial scale is the latest outstanding accomplishment in this field.

Principles.

The fundamental principles of the process are familiar. The article to be plated, after very careful cleaning, is immersed in a solution of the metal of which a coating is desired, together with a piece of the same metal usually, although some insoluble material which is also a good conductor of electricity, for example, graphite, can be used under certain conditions. The solution used is referred to as the electrolyte; the article and the piece of metal, the electrodes. If connection is made to some source of electromotive force, for example, a storage battery or a direct current generator, by means of metallic connections from the two electrodes, a continuous current can be passed through the electrolytic cell. The connection must be such that the article to be plated is the cathode of the electrolytic cell, that is, the electrode by which the current leaves the cell, according to the conventional method of representing the current flow. Under the driving force of the applied electromotive force, metal ions of the electrolyte move toward and finally reach the cathode, where, as the change from the ionic to the atomic or metallic state results by the taking up of the necessary electrons, the electrodeposit is built up. At the surface of the other electrode, provided an electrode of the metal of the same kind as that which is being deposited is used, the opposite change is occurring, metal ions of the same kind as those already in the electrolyte are being formed from the atoms of the metal as each atom loses one or more electrons, according to the kind of metal, and if the process is continued long enough, these

ions will ultimately be transferred through the solution to the cathode, be changed back into atoms and be built into the structure of the deposited coating.

In a few special cases it is not necessary that an external electromotive force be applied to the cell. The metal "plates out" on the cathode directly when immersed in the solution. Ordinarily the deposit is a loose flocculent one, worthless as a coating, but in a very few cases a very thin uniform adherent film is produced which serves well as a decorative coating at least.

The amount of metal deposited on the cathode is proportional to the quantity of electricity used, that is, to the current and the time, but is practically always less than the theoretical amount, since the current efficiency is less than 100 per cent. Any current used for any other purpose than deposition of metal, for example, the discharge of hydrogen on the cathode, is wasted so far as the useful work of electroplating of metal is concerned. With any given fixed plating conditions, the thickness of the deposit is proportional to the period of deposition.

The production of metallic coatings by electroplating is only a part of the much broader subject of electrodeposition. In this book only those features which markedly affect the properties of metallic coatings as produced by electroplating will be discussed. The electrochemical theory underlying the deposition of metals as well as the practical details of plating control, choice of plating baths, and the like do not fall within the scope of this discussion.

In actual practice, the electroplating of metal surfaces is not nearly so simple as might be inferred from the brief description above. The character of the deposit, and hence its usefulness as a metallic coating, varies within very wide limits according to the plating conditions. It is necessary, first of all, that the deposited metal be distributed quite uniformly over the surface to be covered and not in the form of large crystals at a relatively few specially favorable points. Solutions of rather complex composition are often employed in order to accomplish this. It is very essential also that the metal coating be deposited in a dense compact condition. With certain types of solutions or under extreme conditions of deposition, the metal may be deposited in a porous, spongy form, a condition which can be attributed, in many cases, to the formation of the hydroxide (or oxide) of the metal simultaneously with its deposition, and the inclusion of this in the deposited layer. This is particularly true of neutral solutions in which the film of solution adjacent to the cathode readily becomes alkaline as the evolution hydrogen proceeds. If the solution is a dilute one and unagitated, so that the metal ions in the solution film adjacent to the cathode surface are

relatively quickly used up, this tendency toward a spongy deposit is still more pronounced. Evans [N 16] suggests that the relative freedom of cyanide solutions from the tendency toward sponginess of the deposit may be attributed in large measure to the solubility of the hydroxide in the cyanide. Substances such as tartrates and oxalates which are often added to electroplating baths, he suggests, may improve the deposit in a similar manner.

Uniformity of the Deposit.

Failure in any coating in service practically always occurs in areas having less than the average thickness of coating. For any given amount of metal spread out in the form of a coating, the more nearly uniform in thickness the coating is, the greater the life which may be expected of it. Uniformity of thickness is a very desirable feature for all coatings and especially is this feature to be borne in mind in the production of coatings by electrodeposition.

In the simple case of two electrodes of sheet metal placed in a plating bath with the plane sides opposite each other, it is evident that most of the metal will be deposited on that side of the cathode facing the anode, the deposit on the back of the cathode being restricted to a narrow strip along the edges. In practice, care is taken that a condition even approximating this does not obtain. By the proper spacing and placing of the anodes with respect to the articles to be plated such a condition can be obviated to a large extent. The movement of the cathodes in the solution, as in "barrel" plating, goes far to ensure uniformity of distribution of deposited metal over the surface. Most articles which are plated are not of a simple regular shape, however, hence certain parts are nearer to the anode than others. Consequently, on account of their higher current density, such parts receive a somewhat heavier deposit of metal.

In depressions on the cathode surface, that is, recesses, re-entrant angles and so forth, the coating is, as a rule, thinner than on the more exposed parts, particularly on points, corners, and sharp edges. In addition, any condition conducive to a slight roughening of the surface of the deposited film, such as suspended particles lodging on the cathode surface, leads to further unevenness of the deposited coating since any initial roughening tends to increase rather than to be smoothed off.

Solutions of the same metal differ very noticeably in the character of the deposit, especially in uniformity of thickness, produced from them. This difference in behavior of the solutions is designated by the term "throwing power". As a rule, the cyanide solutions have a much higher throwing power than more simple solutions of the same metals.

The throwing power of the solutions of different metals varies decidedly, that of chromium, for example, being very low.

Structure and Other Characteristics of the Coating.

A smooth, strongly adhering coating having relatively high strength and hardness is the desideratum in electroplating. This combination of properties aids greatly in the buffing and polishing of such coatings, which so often form a necessary part of the finishing operation. Any metallurgical means for improving the strength and hardness of any simple metal is essentially a grain-refining process. Electrodeposited metals form no exception to this general rule. Any change in the conditions of deposition which results in the formation of a smaller grain size of the deposited metal improves the properties of the coating, as a rule.

In certain electrolytes, for example cyanide solutions, the deposit is very smooth and normally has an exceedingly fine grain. The use in other baths of "addition agents", which often are of a colloidal nature, aids in the formation of a small grain size in the deposited metal. This result cannot be attributed to any one single cause. One of the most obvious, however, is that some of the colloidal material is built into the structure of the electrodeposit and the smaller grain size results from the "obstructive effect" of this foreign material on the grain growth of the metal, in a manner strictly analogous to obstruction offered by non-metallic inclusions in a metal to grain growth during the annealing of the metal. It is essential that the amount of the added colloid be small since if too much is used the deposit may be very weak and brittle.

Some addition agents which are not colloidal as such probably give rise to a colloid by hydrolysis in the bath. Such is probably the case with aluminum sulfate, additions of which are sometimes used in zinc plating. Small amounts of the colloidal hydroxide are probably formed by hydrolysis.

With any given plating solution, the conditions under which it is operated determine largely, of course, the physical character of the coating deposited. Metal deposited very slowly, with a low current density, is ordinarily coarsely crystalline and relatively soft. An increase in the current density results in a finer-grained and stronger deposit. There is a limit, however, to the current density which may be used, as a rough "burnt" deposit results if the rate of deposition is too great. By changing other conditions, however, such as by using a concentrated solution and agitating the bath, the ill effects of high current density can be overcome in large measure. A decrease in the temperature of the bath or, in fact, any condition which favors the growth of a large number of

grains rather than a relatively few favored ones, results in a finer-grained, stronger and harder deposit. The various factors of bath operation which affect the character of the electrodeposit are so inter-related that the subject is a rather complicated one. Some of the references cited [Bibliography, List N] should be consulted for details and for a more complete discussion of the subject of the control of the properties of electrodeposited coatings.

Adhesion of the Deposit.

The degree of adhesion of the coating to the base is of very considerable importance. The initial cleanliness of the surface to be plated must, of course, be given primary consideration in securing a strongly adhering coating. Even with a *clean* surface, however, the adherence on the rougher parts is generally much better than on the very smooth portions. According to Evans [N 16] certain metals adhere to some better than to others; usually, the adherence is better to a softer than to a harder one, for example, nickel adheres better to lead than to steel. Metals which alloy readily show better adherence than those that do not. The nature of the bond between the coating produced by electrodeposition and the base has been the subject of considerable discussion; an alloying action between the two was early suggested [N 3] as the explanation. An electrodeposited coating is composed of very pure metal, except in the special cases of alloy deposition, and in practically all cases no evidence whatever of such alloying action can be seen in the microstructure of such coatings. If an alloy layer exists in ordinary electroplated coatings, its thickness must be only of atomic dimensions. It has recently been shown that in a few instances, however, (p. 151) evidence has been obtained showing that the crystals of the deposited layer may be formed as direct extensions of the pre-existing crystals of the base metal on which the deposit is laid down if proper precautions are taken. Such a coating would, of course, form an integral part of the article.

The condition of the coating with respect to internal stresses, which may result in cracking and peeling of the coating away from the base, is of considerable importance with certain metals. A completely satisfactory explanation of this phenomenon has not yet been advanced. This condition is most pronounced with metals such as nickel which can be deposited in a relatively hard condition [N 24]; the adsorption of hydrogen by the metal as it is being deposited appears to be responsible, at least in large measure.

Practical Aspects of Electroplating.

In a great many respects, electroplating is an almost ideal method of coating. The ease with which the thickness of a coating may be controlled within very close limits, the ready adaptability of the same apparatus for depositing a coating of different composition, and the ability to work on a very small scale are advantages which are secured by no other current commercial coating method. For small jobs consisting of only a few pieces to be plated the apparatus may be extremely simple. For handling a large number of pieces, particularly relatively small articles of the same shape and size, rather elaborate methods have been perfected. These are of two general types, the "barrel" and the "conveyor", and are used extensively in the zinc-plating industry as explained later in the discussion of this type of coating.

Since electroplated coatings are used in a great many cases for decorative purposes as well as protective, a buffing and polishing treatment is usually given the coating after deposition. This treatment improves the character of the coating as a rule, especially if it is initially somewhat porous, by rendering the surface smoother, and the coating as a whole, denser and more impervious.

Chapter 4.

Metal Spraying and Sprayed-metal Coatings.

The production of metallic coatings by spraying, just as paint, varnish, and similar non-metallic coatings are widely applied, is now a success although its commercial applications, particularly in this country, are limited. The process, which is of comparatively recent origin, is generally referred to by the name of the Swiss Engineer, M. U. Schoop, who has done most to make practicable its commercial application. A good deal has been published concerning the process, but as Hopfelt [K 41] has remarked, many of the things which have been written are more or less "expressions of hope" by the promoter as to the possibilities of the process. As is often the case with new processes, these possibilities have been overstated and the fundamentals and actual accomplishments have not received the attention deserved. On account of the limited commercial applications of metal spraying, the various sprayed-metal coatings will be briefly considered in this chapter instead of in the discussion of commercial coatings which follows.

Development of the Process.

The metal-spraying process is properly to be considered as a development and special application of the very much older processes for powdering or atomizing metals. Methods for producing metal powders for use in gilding were known before the beginning of the Christian era. In all of the older processes, however, the powder was made from the solid metal and only in comparatively recent years have attempts been made to "atomize" the molten metal. In brief, such methods consist in breaking up a thin stream of molten metal into a finely divided condition either by means of a strong blast of air or other gas or by some mechanical device. To Schoop belongs the credit of conceiving the idea of preparing a metal coating by holding the article directly in the path of the atomized metal [K 66, p. 5].

Schoop states [K 22, K 42] that the idea of metal spraying had its inception in his mind on incidentally observing the behavior of lead bullets fired from a small rifle against his garden wall. He believed fusion of the metal by the heat resulting from the transformation of the

kinetic energy of the bullet to be the fundamental characteristic of the process.

An excellent account of the development of the metal-spraying process from its inception to present-day commercial methods has been given by Turner and Budgeon in their recent book on the subject [K 66]. Calder, in a chapter of the book by Flanders on Galvanizing and Tinning [B 27], has well summarized the course of development of the process, however, so far as this country is concerned, by reference to the earlier U. S. patents on the subject. In 1902, Thurston was granted a patent (U. S. Pat. 706,701) for producing a metal coating by impacting metal dust upon a metal base by means of a blast of unheated gas. The process was not successful, primarily because of the lack of heat, and no commercial application was made of it. The liquid metal-spraying process was patented by Schoop (U. S. Pat. 1,128,058) in 1915. A small stream of molten metal issuing from a nozzle attached to a large reservoir of melted metal was broken into a fine spray by a jet of air and deposited as a coating or for copying the object sprayed upon. A patent by Schoop in 1915 (U. S. Pat. 1,128,059) covered a metal dust-spraying process which was very similar to Thurston's except that ignited gas was used. Morf, in his patent of 1905 (U. S. Pat. 1,128,175), covered the process known as the metal wire-spraying process, the metal of a wire being melted, "atomized," and projected upon the base which was to be covered. The apparatus suitable for the process, known as a "pistol", was covered by Morf's patent (U. S. Pat. 1,100,602) of 1914.

The portability of the apparatus, a very necessary feature for the successful use of a process of this kind, was entirely lacking in the early methods. The liquid metal-spraying process involved the use of a reservoir of molten metal which with the auxiliary parts weighed over a ton, the metal dust-spraying apparatus weighed over a hundred pounds, whereas the modern "pistol" weighs between three and four pounds. In the more recent development of the method the pistol has been improved and made even lighter and the application of the electric arc as a source of heat for melting the metal has been utilized (K 29, K 40), thus making the apparatus still more portable.

Operation of the Process.

The present commercial metal-spraying process, both in the United States and abroad, favors the use of the gas-fired spraying pistol rather than the electric pistol, although the latter is now receiving more serious consideration. Figure 4 shows the form of pistol in commercial use in England [K 59] and is typical of the gas-fired pistol. In such instru-

ments, the metal, in the form of wire of rather small diameter, is pushed into the nozzle of the pistol at a constant rate so that as the end of the wire is melted and atomized the position of the end with respect to the flame remains unchanged. The size of the wire used depends upon the metal to be sprayed. According to Turner and Budgeon [K 66, p. 38], the sizes commonly used in England are: tin and lead, 1.5 mm.

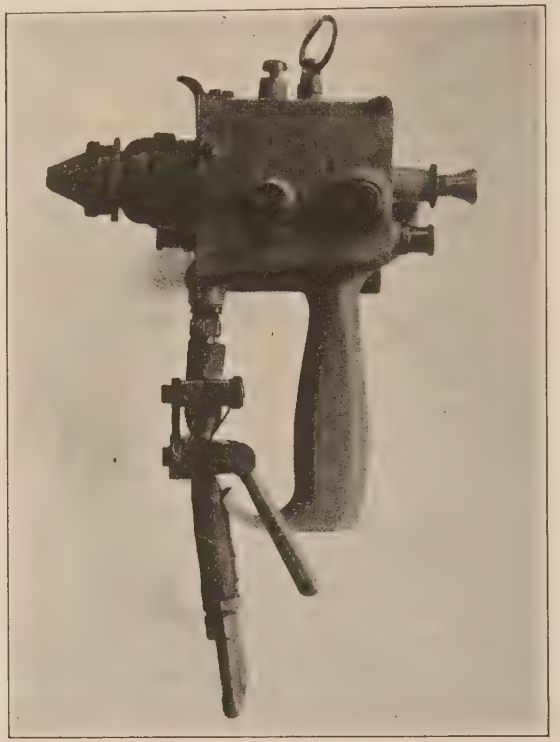

FIG. 4. Metal-spraying pistol, English model [K 59]. The size of the pistol can be estimated from the handle. The wire which is to be atomized and sprayed is fed into the pistol from the right, the gas, oxygen and air for melting, "atomizing" and spraying are led in through the tubes in the lower part.

diameter; aluminum and zinc, 1 mm.; copper, bronze, brass and nickel, 0.8 mm. These are approximately 15, 18, and 20 gage (Brown and Sharpe), respectively.

In its simplest form, the nozzle of the gas-fired pistol may be considered as consisting of three concentric tubes. The wire to be sprayed is advanced through the central one; through the annular space surrounding this central tube the gaseous mixture, either hydrogen or acetylene with oxygen or air, is passed, which upon burning at the

orifice melts the wire in the inner part of the conical flame. Through the second or outer annular space passes the compressed air or other gas which accomplishes the atomizing and spraying of the metal as it is melted. Figure 5 shows this in diagrammatic form.

According to Kasperowicz [K 30] an air-gas flame is sufficiently hot to spray zinc, lead or tin. For such metals as iron and nickel the oxy-hydrogen flame is used and for those of still higher melting points the oxy-acetylene flame is necessary.

Attempts to use fairly large wires in the gas-fired pistol of the usual design, and hence spray at a faster rate, have not been very successful [K 60]. With the electric pistol, however, it has been possible,

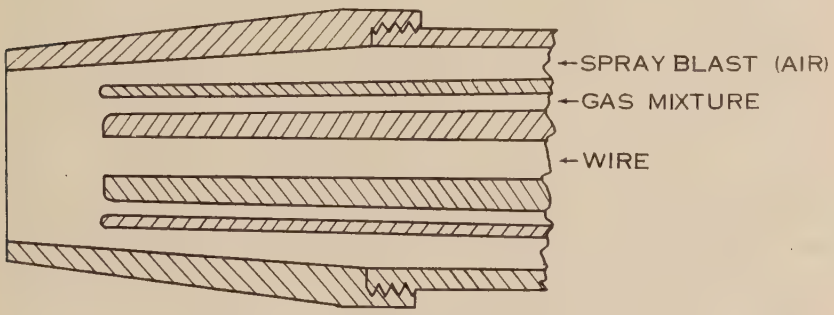

FIG. 5. Essential features of the nozzle of a metal-spraying pistol in which gas is used for melting the metal wire.

on an experimental scale, to overcome this difficulty and to use wires, at least of the metals of lower melting point, such as zinc, considerably larger than has been the practice hitherto.

The driving mechanism for feeding the wire, usually a small air turbine driven by the compressed gas used for spraying the metal, and other mechanical features of the pistol are of interest, but are not essential in a discussion of the nature of the coatings produced.

The electrically operated pistol naturally differs considerably in its construction and operation. Efforts to use but a single wire of the metal to be sprayed [K 29] in such a pistol have not been successful. Two wires are used which for a portion of their length conduct the current, and the heat which melts the metal is produced by the arcing between the two, at the ends, similar to the action between the two carbon electrodes in the familiar arc lamp. Compressed air or some inert gas is used for breaking up the drops of metal in a very finely divided form and projecting this metal cloud or mist in the form of a spray. Any of the common metals available in the form of wire which can be melted in

the oxy-hydrogen flame, with one exception, magnesium, can be used for producing a coating by spraying.

A device for the semi-automatic metal spraying of small articles, which are not too complicated in shape, within a closed cabinet is now available on the market abroad [K 41]. The articles are moved about and their position changed with respect to the spraying nozzles so that a satisfactory coating can be produced in 10 to 20 minutes. Many of these devices are arranged for the preheating of the articles before spraying and for rumbling them after spraying. For articles whose shape renders them suitable for coating by such treatment, the method is decidedly satisfactory.

The metal-spraying process in which metal dust is used still finds considerable commercial application. It is usually referred to as the "cyclone" or "gravitas" process. The finely divided metal is heated by passing the stream through the flame of the blowpipe. The coating produced is essentially the same in character as that made by the other process. This process is used more for spraying zinc than for other metals, since zinc can be secured in the form of powder as a by-product from zinc smelters reasonably cheap, whereas manufactured metal powders are expensive. Nicolardot [K 46] has also pointed out a serious objection to the use of manufactured metal powders. Their preparation involves the use of grease of some kind and much of this is retained on the powder. On heating, the greasy matter partially burns and produces carbon which prevents the formation of satisfactory coatings.

Importance of Proper Preparation of Surface for Adhesion of Coating.

Practically all who have studied the subject of sprayed-metal coatings agree that the preliminary preparation of the surface to be sprayed determines in very large measure the degree of adherence of the coating. Sand blasting is, without exception, recommended as a very suitable, if not the best, method for the preliminary treatment since it leaves the surface roughened ready for the deposit and no drying or further treatment is required as would be the case with any chemical treatment such as etching, although the latter can be used. The adherence of the coating to the base is without doubt largely mechanical.

Adherence is also improved if the base is preheated somewhat. This can be done either by heating the entire article before spraying or by playing a flame over the surface just before the metal spray is applied. In some commercial forms of metal-spraying apparatus a set of gas burners surrounds the orifice of the metal-spraying pistol so that the

surface is heated as it is sprayed. Preheating of the surface is especially desirable when thick coatings are to be sprayed. The temperature to which the surface is preheated according to some [K 66, p. 91] should be above 250° C. (490° F.). If the temperature is maintained as high as, or somewhat higher than, this, there is a chance for slight alloying between the metal of the coating and of the base, for certain metals—a condition which does not obtain at all if the surface is not heated.

Structure of Sprayed-Metal Coatings.

Arnold [K 23] has shown mathematically that Schoop's original concept of the fusion of the particles at the instant of impact is untenable. In addition to showing the approximate velocity which would be required to accomplish this result, he has also demonstrated that a decided increase in the velocity of the particles sprayed must accompany an increase in the melting point of the metal to be sprayed. This is not borne out in practice.

Recently Turner and Ballard [K 59] concluded from the results obtained in the microscopic study of metals sprayed upon glass that the metal is still molten, or at least very plastic, as it strikes the surface to be sprayed. Their micrographs indicate that a spattering of the metal occurs upon impact, the appearance being very similar to that of a rain drop striking against a glass surface although, of course, on a microscopic scale. The best results were obtained with nickel, copper, and aluminum sprayed upon glass heated to 400° C., although zinc, lead, and tin gave indications of the same phenomenon. Figure 6 shows the appearance of copper, aluminum and lead sprayed upon glass.

It may be concluded on the basis of these observations that the individual metal particles upon striking the surface to be covered are flattened into relatively thin scales, thus increasing the "covering power" of the metal. A condition of slight porosity in a metal-sprayed coating therefore does not necessarily indicate perforation of the coating.

The well known fact that metal can be sprayed upon paper and other combustible materials without any trace of scorching and also upon the hand at a distance of 10 to 12 inches from the nozzle without any marked ill effect makes the acceptance of the conclusion that the particles are molten at the instance of impact somewhat more difficult than if this were not the case.

The microstructure of sprayed coatings has been described and illustrated by Arnold [K 23, 24]; Nicolardot [K 46]; Turner and Ballard [K 59]; Rawdon [B 113] and others. All agree that no alloying action between the metal of the coating and that of the base metal can be detected in the microstructure as ordinarily examined.

FIG. 6. Metal particles sprayed on glass, × 50 [K 59].

A, lead sprayed on cold glass.
B, lead sprayed on glass which had previously been heated to 400°C.
C, aluminum sprayed on cold glass.
D, aluminum sprayed on glass heated to 400°C.
E, copper sprayed on cold glass.
F, copper sprayed on glass heated to 400°C.

Guilbert [K 56], however, in a recent article claimed that an alloying between coating metal and base must take place although no proof of this was given. The sprayed coating, irrespective of the metal used, has a characteristic laminated structure or stratified appearance as seen

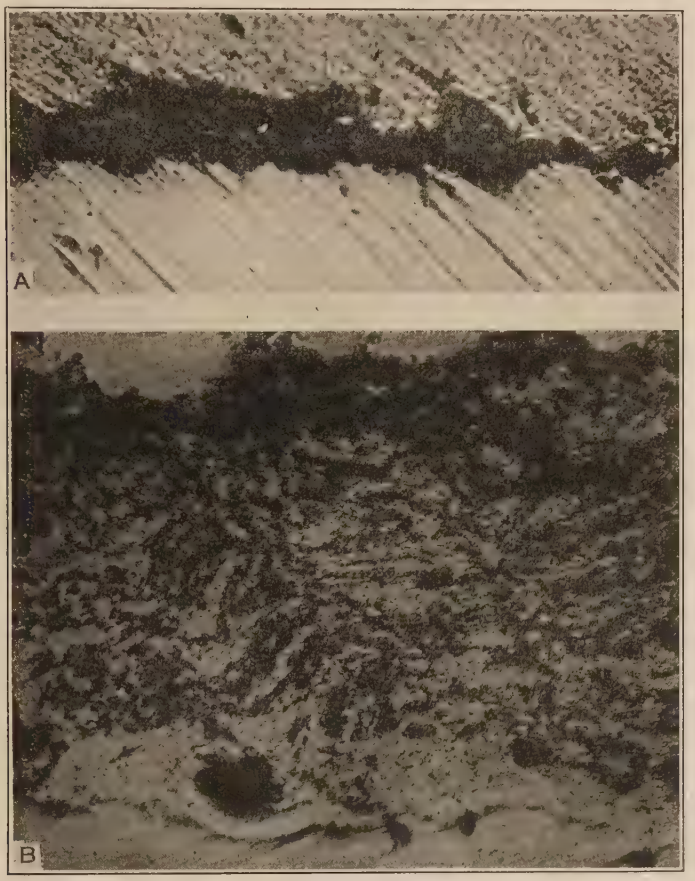

FIG. 7. Microstructure of a metal-sprayed zinc coating, × 500 [B 113, M 19].
A, a very thin coating produced by "playing" the spray over the surface once; the dark irregular layer is the sprayed zinc.
B, heavy zinc coating produced by spraying the same area several times. Note the pronounced stratified condition.

in cross section. This is shown in Figure 7. The stratified condition of the coatings is usually considered to be an oxidation effect and in coatings sprayed by means of an inert gas this feature is very much less pronounced than in those sprayed by means of compressed air. By annealing sprayed copper coatings *in vacuo* at a sufficiently high tem-

perature to permit coalescence of the oxide particles to a size sufficiently large to render the identification sure, Arnold has shown conclusively that the stratification is related to oxidation. He suggests that the oxidation may occur within the oxy-hydrogen flame itself rather than be produced by the compressed air used for spraying. However, this would not account for the fact that certain layers of the coating are higher in oxide than others, nor that oxide may occur in electrically sprayed coatings, especially if sprayed with compressed air. In the outer part of the conical-shaped spray conditions for oxidation undoubtedly are much better than in the interior, and as the spray is played back and forth over the surface to be sprayed the oxide is concentrated in films rather than being uniformly disseminated throughout the entire thickness of the coating.

Arnold [K 23] has shown that in coatings produced by spraying successively two different metals, for example, zinc and copper, no evidence of alloying of the two into brass could be detected in the microstructure. Schoop [K 35], however, says that the use of the electric spraying pistol, in which the two wires of different kind may be used, an alloy can easily be formed, for example, brass, by using copper and zinc wires. Recent examination at the Bureau of Standards by the x-ray method of deposits made by spraying zinc and copper simultaneously has shown that some alloying of the two metals does occur. Zinc and copper were also detected in considerable amounts in the deposit, however, so that it would appear that the formation of a brass coating by the simultaneous spraying of zinc and copper is not so simple as has been claimed.

Physical Properties of Sprayed Metal.

One of the principal advantages of the metal-spraying process is that the coatings are produced upon the finished article. The properties of the deposited metal are therefore of somewhat less importance than is the case for materials such as coated sheets which often must be fabricated into the finished article subsequently to coating.

Invariably, the density of the sprayed metal has been found to be somewhat less than that of the same metal in its cast state before spraying. This difference is to be attributed at least in part to the oxidation which may accompany the spraying and not entirely to porosity, gas cavities and the like, as is the case with ordinary cast metals. By the improved methods of spraying now in use, especially by the use of an inert or non-oxidizing gas for spraying, the density of the sprayed metal can be increased considerably so that it compares very favorably with the same metal before spraying. The density of the sprayed metal can also be increased by such processes as scratch brushing, buffing and

TABLE 2.—DENSITY OF SPRAYED METALS AS COMPARED WITH THE DENSITY OF THE METALS IN ORDINARY FORM.

Metal	Turner and Ballard [K 59]	Arnold [K 23]	International Critical Tables 1926
			Grams per cubic centimeter, at 20° C.
Aluminum	2.4	2.31	2.70
Zinc	6.4	6.32	7.14
Tin	7.1	6.82	7.31
Iron	6.5	...	7.86
Copper	8.0	7.51	8.92
Lead	...	9.77	11.34

polishing, which are often resorted to for improving the appearance of sprayed-metal coatings.

In Table 2 are given results which have been reported for the density of various metals after spraying.

A considerable difference of opinion exists concerning the degree of porosity of sprayed-metal coatings. Such coatings, according to Hopfelt [K 41, K 55], as ordinarily produced are practically always porous to the extent of allowing moisture to creep in under atmospheric pressure. However, by using an inert gas instead of compressed air for spraying, the porosity may be reduced very materially, at least for the metals of lower melting point. Turner and Ballard [K 59] state that by skillful and careful manipulation of the air pressures in the ordinary method, coatings of lead, tin, and zinc which are impervious to liquids can be produced. They cite the illustration of the spraying of sticks of sodium with lead and tin, the coating being so impervious that no chemical action resulted when the sprayed sodium was thrown into water. They were unable, however, to make absolutely impervious coatings of copper, aluminum, or brass by the ordinary methods of spraying.

Values for the hardness of sprayed metals have been reported. Arnold [K 23] has given results obtained with the scratch hardness method showing that, with a few exceptions, the scratch hardness of the sprayed metal is considerably less than that of the same metal in the cast form. Differences as great as 35 or 40 per cent were noted. More recently, Turner and Ballard [K 59] reported hardness results obtained with specimens sprayed by improved methods showing that the sprayed metal, as measured by the scratch method as well as the scleroscope, was harder than the same metal in the cast condition. However, with the ball-indentation method no pronounced differences

in hardness were found for the metals as sprayed or as cast in the ordinary manner. The specimens for the hardness tests by the ball-indentation and the scleroscope methods were built up by continuous spraying upon a small area until a volume of metal suitable for these tests was secured.

Tension and notched-bar impact tests of specimens built up entirely by metal spraying have been reported by Turner and Ballard. The ductility and impact resistance of such specimens were found to be relatively very low, as might be predicted.

Various treatments are used for improving the character of a sprayed coating. The advantage of heating the object to be sprayed has been referred to above. The adherence of the coating to the base will usually permit the use of some mechanical means for reducing the porosity, such as wire brushing, polishing, and blasting with ball shot and the like. This of course adds to the expense and obviously such methods are applicable principally to small objects. In the case of sprayed coatings of zinc and cadmium, the porosity of the coating need not cause nearly so much concern as with such metals as copper or nickel, since each of the metals, zinc and cadmium, is anodic toward iron when the two are in contact and immersed in an electrolyte. A coating can be made less porous also by chemical precipitation within the pores of the coat. Sprayed lead coatings can be made very impervious to chemical attack by means of a preliminary treatment whereby lead sulfate is formed within the pores of the lead coating [K 55].

Porosity in a metal-sprayed coating may also be overcome by using some other metal either as the initial or as an intermediate layer, somewhat similar to the practice in nickel plating of using a copper layer "sandwiched" between two nickel layers. Turner and Budgeon [K 66, p. 103] have reported that sprayed coatings of brass, copper, or nickel can be made very solid by using an intermediate layer of tin and heating, after coating, to a temperature somewhat above the melting point of tin.

Practical Applications of Metal Spraying.

As is often the case with new processes differing decidedly in principle and mode of operation from the better-known processes in current use, many of the early predictions relative to the use and applicability of metal spraying have not been realized in practice. Apparently, too often the mistake was made of advocating the use of the new process to replace older satisfactory methods in use rather than to emphasize the inherent unique characteristics of the process which admirably fit it for certain applications practically unattainable by any other means. The application of coatings *in situ,* that is, to the finished

article, which is so characteristic of the metal-spraying process, is true for no other metal-coating method, on any very large scale.

The amount of metal added as a coating by metal spraying can be controlled within rather narrow limits. In this respect the method is excelled only by electroplating. The coating may vary from a very thin film forming a suitable surface for holding a paint coat (which has been advocated, as economical and feasible) to relatively thick coatings, for example, several millimeters thick, for the protection of chemical equipment.

Another very valuable feature of the process is the control of the composition of the coating. Not only may coatings of the purest metal available be applied, approaching thus the results of the electroplating method, but two metals may be applied simultaneously or successively without any inconvenience or delay. For example, a combination of zinc and aluminum (a coating of zinc followed by one of aluminum) has been found [K 60] very suitable for resisting the corrosive attack of atmospheres high in sulfur dioxide.

A sprayed coating as a rule is very uniformly distributed both in the depressions as well as on elevations. If for any reason a thicker coating is desired on certain parts, such as those exposed to wear, than on others, this is readily accomplished.

The metal-spraying process has been used to a considerable extent abroad, especially in Germany and France, for the zinc coating of large constructions, and such applications have definitely passed the experimental stage. Included among such large-scale applications are the zinc coating of towers for electrical transmission lines and radio stations, the spraying of the hulls of ships, of dock gates, of bridges and tunnel construction, and of the entire under framework of street cars, as well as tank cars and large storage tanks [K 66]. In all such cases, the surface must be prepared by sand blasting before it is sprayed. This adds considerably to the cost but the claim is made that the long life of such coatings compensates for the higher initial cost. The fact that all rivet and bolt heads as well as all cut edges are coated is of very considerable importance. The excellent "paint holding" properties of a sprayed-zinc coating as compared with those of a galvanized coating is also decidedly in favor of the spraying process for those constructions which are to be painted.

The small scale applications of metal spraying are exceedingly varied and numerous. Many such applications are for ornamentation. This was true especially in the early development of the process since it can be applied to such materials as wood, paper, textiles, etc. The use of metal spraying as a supplement to other coating processes is of interest.

For example, sherardized castings not infrequently show spots where the coating is either very thin or lacking entirely. Such areas can be easily and quickly covered by metal spraying and rejections because of imperfect coatings can be almost entirely eliminated.

The use of the process in connection with the carburization of steel has already been referred to. Guillet and Bernard [D 20] have shown that a layer of sprayed copper 0.02 to 0.04 mm. thick offers ample resistance to the penetration of carburizing gases at 1000° C., and hence can be used for coating those portions of a steel article which are to remain soft after the case-hardening process.

The use of the metal-spraying process for the coating of aluminum with other metals and for the production of aluminum coatings on other metals constitutes one of the most important applications of this process. Coatings of pure aluminum can be obtained in almost no other way. Such coatings are being used to a moderate extent with pronounced success for the protection of grate bars and other furnace parts at elevated temperatures [I 20]. When heated such coatings form a tough adherent oxide layer; alloying with the base metal also occurs. It may be considered, therefore, that a calorized layer is produced. The life of such sprayed aluminum coatings is very much less than that of the regular calorized product but likewise the initial cost and the cost of renewal is correspondingly much less.

The successful coating of aluminum with another metal is a matter of considerable difficulty. Electroplating of aluminum is the only method other than metal spraying that can be depended upon except for simple shapes such as sheets and most electroplated aluminum has not proved satisfactory when exposed to severely corrosive conditions. The protection of aluminum and light aluminum alloys against atmospheric corrosion is a problem of increasing importance as the development of aircraft progresses. The use of metal-sprayed coatings on such parts appears very promising. Duralumin or other alloys which must be heat-treated in order to develop their highest tensile properties can be heat-treated after being sand-blasted and metal-sprayed. This, incidentally, removes the undesirable effect of the sand-blasting process.

Lead coatings are another type of coating for which the metal-spraying process is admirable. The use of this process for the lead coating of chemical equipment constitutes another very important application of the process [K 66, p. 148].

On the whole, it seems that the metal-spraying process has not yet settled down into its proper place. This is only a matter of time, however, since the value, importance and practicability for many purposes of the metal-spray method has been demonstrated again and again.

Chapter 5.

Chemical Treatment of Metallic Surfaces.

Production of Coatings.

It is a well established fact that the corrosion resistance of many metals is dependent, in large measure, upon the surface-oxidation film which forms as a result of an initial corrosive attack. The more continuous and adherent the corrosion film, the greater is the degree of protection given to the underlying metal. It is very generally recognized that the relatively high resistance of aluminum, for example, to ordinary atmospheric corrosive attack is largely a function of the very thin but extremely tenacious and continuous coating film, presumably of oxide, which soon forms on any freshly polished surface when exposed, especially in a damp atmosphere. It has recently been shown by Vernon [L 24] that polished copper which has been heated somewhat, for example, one hour at 75° C., shows a decidedly greater resistance to ordinary atmospheric corrosion than does a similar polished specimen which has not been heated. The surface film of oxide which forms, though invisible, is sufficient to protect the metal very effectively against subsequent attack. Vernon concludes from theoretical considerations that the minimum thickness of a protective oxide film (on copper) in order to be really effective against corrosion, must be such that the unit lattice of the oxide is completed over the whole of the surface. It has recently been shown [L 27a, L 44b] that the film to which the passivity of certain metals is to be attributed can be removed from the surface and its nature and properties studied.

Numerous methods based upon this principle of an initial chemical attack of the surface metal are used for the production of protective coatings. Such coatings cannot be designated as "metallic", since no metal is added to the surface. The coating is formed simply as a result of the chemical reaction with the base metal itself. Such a coating is quite different, however, from those of an entirely foreign origin, such as enamels, paints, and lacquers.

The methods in most common use depend upon an oxidizing of the surface of the metal, which is usually iron or steel, the conditions being so regulated that a very adherent oxide coating forms. If the surface

is very clean and polished, simple heating is often sufficient. Chemical oxidation by means of suitable solutions is often employed and recently "anodic oxidation" has come into prominence. This consists in making the article to be treated the anode of a suitable electrolytic cell.

All such coatings are protective only in a mechanical way, that is, by excluding moisture and air from the underlying metal. The continuity of such coatings and their freedom from scratches and other abrasions is an important factor in determining their usefulness. Many of these coatings receive a final oiling which not only adds to their attractiveness but increases their useful life very greatly. The methods used for the production of these coatings are discussed in Chapter 12.

Surface Cleaning Prior to Coating.

Cleaning a metal surface prior to coating is a necessary preliminary in all coating methods. It is essential that the surface be freed from any substance which would prevent the coating metal from coming into *intimate* contact with the base. Such substances are usually either of the nature of grease or an oxide scale, and the cleaning method used is chosen accordingly.

Solvents such as gasoline and benzine and hot alkaline solutions are used to remove grease. Electrolytic cleansing is also used with good results, the specimen being used as the cathode in some solution which, when electrolyzed, forms a film of alkali over the cathode surface. The evolution of hydrogen also aids materially in the removal of the film of grease and its saponification by the alkali.

Oxide scale is often removed mechanically from heavy pieces by blasting with sand or steel shot, by wire brushing in some cases, and in some special cases by tumbling in wet sand. Pickling or removal of oxide by means of acids is a much more widely used method, however. The materials, for example steel sheets, are immersed in a warm acid solution, sulfuric or hydrochloric, and agitated so as to cause the scale as it becomes loose to be detached from the surface. The process is therefore both chemical and mechanical.

Electrolytic cleaning is also used for removal of scale and may be either anodic, in which case the action is largely mechanical in nature, or cathodic in which the scale is detached both mechanically by the hydrogen bubbles and chemically to some extent by the reduction of oxide by the hydrogen.

The general subject of the cleaning of metals, though necessarily intimately related to the metal-coating process, is a subject outside of the scope of this book. Reference should be made to some of the references given on this subject [Bibliography list O].

Chapter 6.

Zinc-coating by the Hot-dipping or Galvanizing Process.

Terminology.

The term "galvanized" as applied to zinc-coated iron had its origin in the concept of the "galvanic" (electrochemical) protection from corrosion afforded iron by zinc in contact with it. Having been used since the early part of the 19th century in referring to such products, it has come to be rather firmly fixed as a commercial term. By some, the term is used as descriptive of only those products coated by the hot-dipping process while others use it when referring to any type of zinc coatings, although a restriction is sometimes made according to the different processes, for example, "cold", "wet", or "electro" galvanizing, for the electroplating, and "dry" galvanizing for the cementation or "sherardizing" process.

Recently the American Zinc Institute [B 30] has advocated strongly that the use of the term "galvanized" be discontinued and in its place "zinc-coated" be used. In this book the term "zinc-coated" will be used as descriptive of all articles coated with zinc irrespective of the process by which the coating may be applied, also irrespective of whether or not the zinc of the coating becomes alloyed with the base, as happens in some of the processes, in which case the coating can no longer strictly be referred to as "zinc". The term "galvanize", as used here, will be restricted to the process by which a zinc coating is produced by immersion in molten zinc, a process which might well be referred to as "zinc-dipping" in order to distinguish it from the other zinc-coating methods.

The use of the English equivalent of the German verb, *verzinken,* and of the French, *zinguer,* has not met with favor as yet as a commercial or trade term.

History of Zinc and the Zinc-dipping Process.

Zinc was not unknown to the ancients; zinc bracelets have been found in the ruins of Cameros dating from 500 B.C. [B 6, B 7], and certain passages of the writings of Strabo 63 B.C.-24 A.D.) in

which "mock-silver" is mentioned seem to refer to zinc. The German philosopher Albertus Magnus, who died in 1280, is stated to have been the first of the more modern writers to mention zinc in his writings, and Paracelsus (1493-1541) was the first to class it among the metals, the name "zinken" being used. The production of zinc by distillation from calamine was carried out by Kenkel in 1741 and Von Swab in 1742, and the production of the metal on a commercial scale was undertaken in England at Bristol in 1743 [B 48]. There is evidence indicating that zinc was known and produced in the East long before it was in Europe. Moulden [B 13] cites the story of the capture by the Dutch of a Portuguese ship laden with a cargo of zinc secured in the East in 1640. The name "spailter" or "spiauter" used for the cargo is suggestive of the commercial term spelter still widely used for cast or slab zinc.

The very complete account of the historical development of the zinc-coating process given by Sang [B 48] has been used freely in preparing the following résumé of the process.

The first recorded experiments for producing zinc coatings by the dipping method are those of a French chemist, Melouin, in 1741. Tinned iron was already known at that time and Melouin attempted to zinc-coat iron sheets in a similar manner by immersion in a bath of molten zinc. The results of his experiments formed the basis of a report to the Académie Royale in 1742. Jean-Baptiste Kemerlin attempted to apply this process for coating kitchen utensils and the like in 1742, and by 1778 the use of zinc-coated iron utensils seems to have been fairly well known in parts of France.

In the description of the process given by Bishop Watson ("Chemical Essays," 1786), sal ammoniac (ammonium chloride) was said to have been used [B 92]. Sang [B 48], however, credits Bauschaendorf of Leipzig (1802) with having brought about the change from the use of a resinous flux to that of ammonium chloride. Bauschaendorf also recommended the use of a preliminary tin coating before immersion in the molten zinc, a practice which, although very early discarded, still survives in the usual dictionary definition of the process today.

Sorel in 1836 was granted a French patent for a zinc-coating process which had practically all the essentials of the process as it is known today. The articles were to be cleaned in dilute sulfuric acid (9% by volume), washed in water for 12 or 14 hours, then put in dilute hydrochloric acid and, after drying, immersed in a bath of molten zinc which was kept covered with a layer of ammonium chloride. On being taken out of the zinc bath the articles were to be well shaken so as to remove excess metal and then plunged into cold water, after which they

might be rubbed with sand and dried. The Sorel process was investigated by the French naval authorities and a very favorable report rendered concerning the protection from corrosion rendered to iron by being treated in this manner. At nearly the same time, 1837, an English patent was granted to H. W. Crawford for a very similar zinc-coating process by hot-dipping which made use of ammonium chloride as a flux. A previous English patent granted in 1805 to Hobson, Sylvester, and Morehouse [B 92], which covered a method for coating iron with sheet zinc for the purpose of corrosion protection, may be cited as illustrating the importance attached to zinc as a protective metallic coating. The commercial development of the zinc-coating industry in England and in the United States is generally conceded to be the outgrowth of Crawford's patent rather than of Sorel's.

The coating of wire with zinc was one of the first large-scale commercial applications of the zinc-coating process carried out mechanically. The coating of sheets was done entirely by hand in the early days of the industry. The patent of Morewood and Rogers in 1846 [B 48] marks the first advance in the sheet-coating industry, in that mechanical regulation of the thickness and uniformity of the coating by means of rolls was attempted. They also recommended the use of an initial coating of tin to precede zinc coating, as had Bauschaendorf previously. Experience showed, however, that the use of a preliminary tin layer was of no advantage and in fact was detrimental, so that it was gradually discontinued.

The success attained with the use of the coating machine for tinplate, about 1863, stimulated action in the zinc-coating industry but, primarily on account of the very much larger sheets which had to be handled, it was not until a number of years later that a real solution of the problem was attained.

Outline of the Hot-dipping Process.

The hot-dipping process for covering metal products with metal coatings in theory is very simple. The article to be coated is properly cleaned and then completely immersed in the hot metal and withdrawn with enough of the molten metal adhering as a surface film to give it the desired coat. In practice the process is not so simple, even with hand dipping. The preliminary cleaning of the metal products to be coated, the fluxing of the surface of the bath of molten metal, the regulation of the bath temperature and the use of addition agents in the metal are important factors, each of which has a bearing on the quality of the coating produced.

The dipping process as practiced for the production of zinc coatings

is entirely manual for irregularly shaped articles such as structural parts, castings, bolts, nuts, nails and similar hardware, fabricated articles as ash cans, laundry tubs, vats, tanks, and pails. Pipes are also, for the most part, dipped by hand. The dipping of materials of regular shape, sheets, wire, woven wire fencing, etc., is done by means of machines.

Cleaning of the Base Surface.

The cleaning of the surface of the materials prior to being coated is a very necessary operation. Although this cleaning operation is not a part of the actual coating process, the degree of success attained in the latter is determined perhaps more by this feature of operation than by any other. The cleaning of steel sheets which are to be zinc coated may be used here as a typical illustration. The pickling is carried out in two operations. In the first the black sheets, suitably spaced in a basket of some alloy resistant to the action of the acid, such as aluminum bronze, are treated with dilute sulfuric acid in a wooden tank. The solution is kept warm either by coils of lead pipe through which steam is passed or by jets of steam in the solution. White [B 114] states that for most purposes a 7.5 per cent solution at 150° C. answers very nicely. Camp and Francis [B 95] state that a 7 per cent solution at 140° to 200° F. for 15 or 20 minutes represents average pickling conditions for sheets. A surging of the solution up and down and between the sheets is necessary so as to aid mechanically in the removal of the scale as it becomes loosened by the chemical action of the acid on the steel. This is often accomplished by moving the sheets up and down in the solution. The time necessary for the complete removal of the oxide scale varies somewhat and rather close inspection is necessary. "Over-pickling" is especially to be avoided [B 65, 95, 114] while "under-pickling" means incomplete cleaning of the surface and hence defects in the metal coating applied to such sheets.

The sheets after sufficient pickling are transferred to another tank in which they are washed with water. They are stored in a tank under water, often for 24 hours or so until ready to be coated. Immediately prior to coating, the sheets are immersed for a very short period (a few seconds) in the second pickling solution, sometimes called the fluxing bath, in which dilute hydrochloric acid is used. In the hand dipping of pieces of irregular shape the articles are thoroughly dried at this stage before being put into the metal bath. In the machine zinc-coating process some of the excess moisture is sometimes removed by rubber rolls before the sheets pass through the flux on their way to the zinc bath. The hydrochloric acid bath very effectively removes any slight coating of rust on the sheets.

The same general cleaning method, differing somewhat in mechanical details, is used for wire, pipe and other steel and iron products. For castings, dilute hydrofluoric acid (approximately 5%) is often used [B 54] for the first cleaning bath in order to remove the grains of sand adhering to the surface. Zinc chloride is widely used as the fluxing solution in the galvanizing of wire.

Numerous addition agents for the pickling baths are on the market. These are intended principally for retarding the chemical attack upon the metal without retarding, however, the rate of the removal of the oxide scale. They also tend to promote a uniform surface attack. Most of these are of a colloidal nature and many are of doubtful value.

The Molten Metal Bath.

A zinc-coating bath, to be successful, should be run on a rather large scale. The ordinary bath used for coating steel sheets contains approximately 30 tons of molten zinc [B 92], and "pots" containing as much as 75 tons are not uncommon [B 95]. The container used is either of open-hearth iron or a low-carbon steel plate, either riveted or welded together. Cast containers are used only for very small jobs. A coke fire was formerly used almost exclusively as the source of heat, but coal has now, to a large extent, replaced it as a solid fuel, and

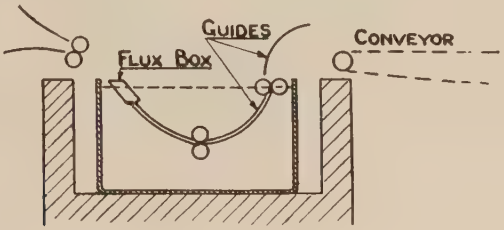

Fig. 8. Diagram of the machine used in the zinc-coating of sheets [B 37].

natural gas is used considerably in this country. In the large installations the heat is transferred to the metal bath through the sides of the container rather than through the bottom. For the coating of sheets a machine shown diagrammatically in Figure 8 and illustrated in Figure 9 is partially immersed in the molten zinc. Likewise, in the coating of wire part of the mechanism is beneath the surface of the metal bath.

Use of lead.—In many instances, a layer of lead 6 to 8 inches or more deep is used in the bottom of the zinc bath. The two metals, zinc and lead, are miscible only to a very slight extent (*See* Fig. 10). The main purpose served by the lead layer is to prevent overheating of the

lower walls of the container, particularly when the pot is first started, and to reduce the attack of the zinc upon the hot walls of the container thus adding to its life and also cutting down the amount of zinc-iron alloy, or dross, formed. It also serves as a cushion upon which the dross floats, which aids materially when the dross is removed. If lead is not added as such to the molten zinc, it is practically always present in appreciable quantity in the slab zinc used so that a lead layer gradually forms in the bottom of the pot.

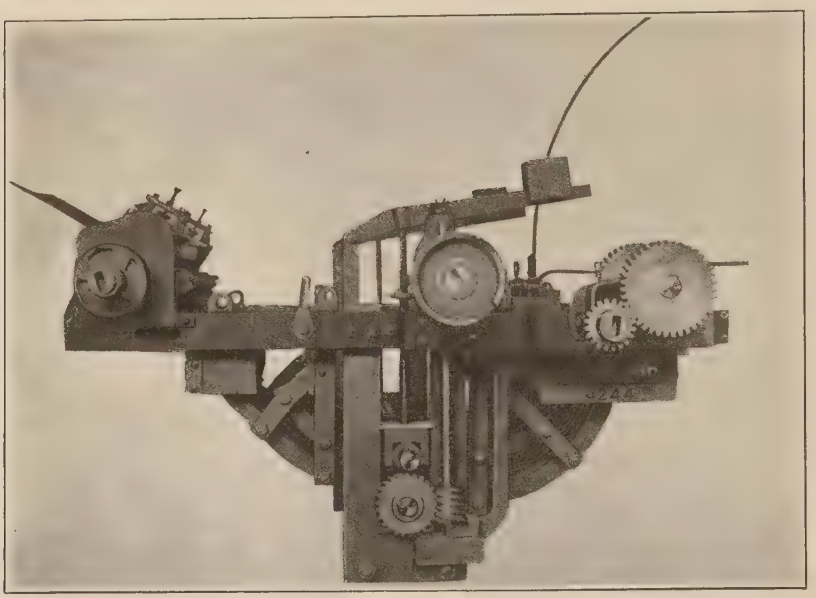

FIG. 9. Present-day machine used in zinc-coating sheets, side view (United Engineering and Foundry Co.).

Formation of iron-zinc alloy or dross.—It has already been pointed out that a necessary condition for coating metals by hot-dipping is an alloying action between the molten metal and the base. Immediately the steel or iron article to be coated is passed into the molten zinc and is heated to the temperature of the molten zinc, some of the iron at the surface is dissolved by the zinc. As will be shown later, the coating produced is far from being a simple layer of zinc but is rather complex and consists essentially of two rather sharply defined layers. The inner or alloy layer has a higher fusion point than the outer one which is essentially zinc. The properties of the coating are very materially affected by this structural condition.

Naturally the walls of the container as well as all iron and steel

parts immersed in the zinc bath are subject to attack by the molten zinc, so that the bath soon becomes saturated with iron. The action of the zinc on any iron chloride carried over from the second pickling bath constitutes another very appreciable source of alloy (dross) formation. According to the equilibrium diagram of iron and zinc (Fig. 11) as given by Peirce [B 117], at 450° C. the saturation point or limit of solubility of iron in molten zinc is approximately 0.10 per cent of iron. The earlier investigators placed the solubility limit of iron in molten zinc considerably higher than this. Peirce's modification of the iron-zinc diagram seems to have been based largely upon the study of the solidified alloys so that in all probability the solubility of iron in molten

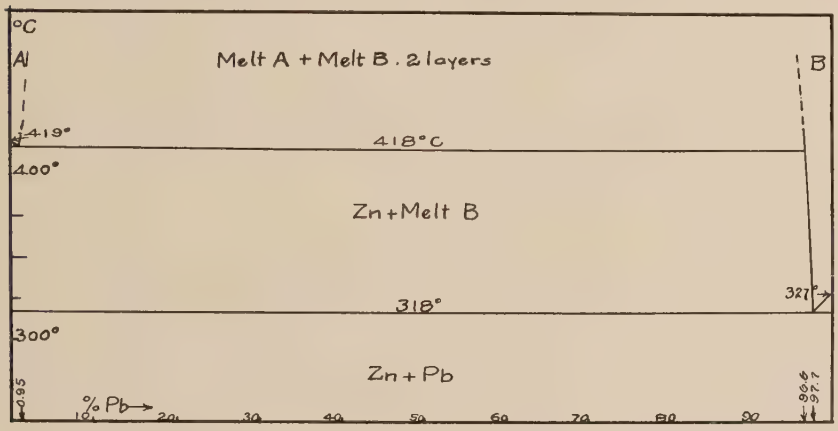

FIG. 10. Equilibrium diagram of the lead-zinc series of alloys.

zinc is slightly greater than he places it. As the amount of iron in the zinc bath is increased beyond the solubility limit, crystals of the iron-zinc alloy, represented approximately by the formula $FeZn_7$ (10.9% Fe) crystallize out of the molten metal, and since they are of slightly greater density than the zinc, they slowly settle to the bottom of the zinc and float on the molten lead. The alloy-rich layer which forms is termed dross.

According to Sang [B 48], the iron content of a galvanizing bath should not be allowed to exceed 0.2 per cent for successful operation. Bablik [B 83] has published data indicating how the weight of coating increases with the iron content of the bath. Such statements were evidently based upon information obtained from small hand-dipping installations in which the chances for a higher iron content as a result of particles of the alloy being held in suspension in the molten zinc bath are very much greater than in a large mechanically operated installation

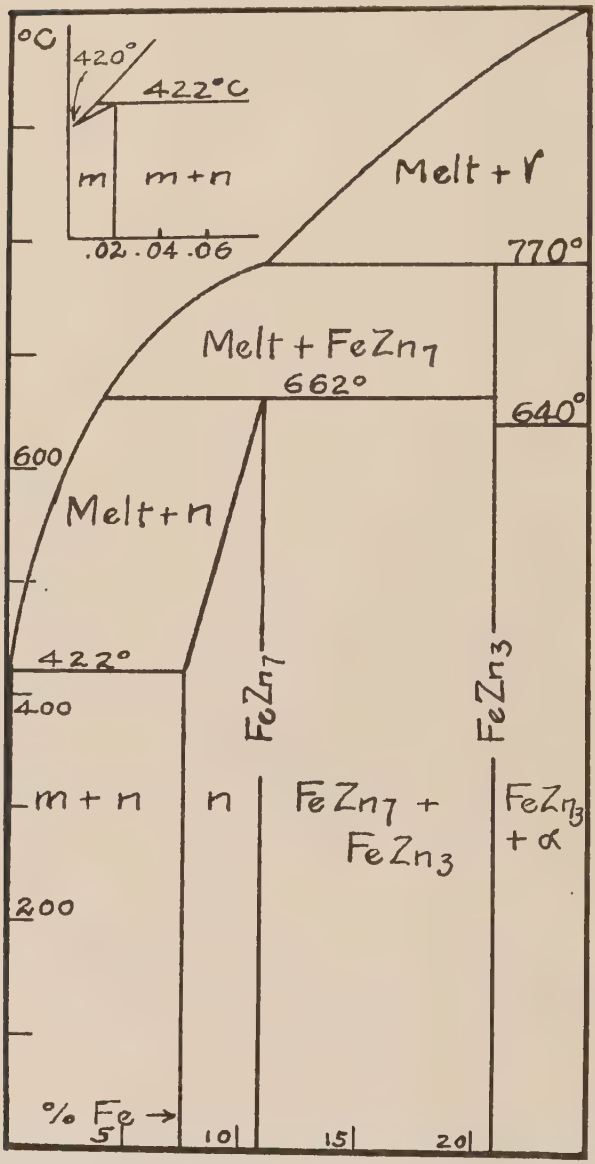

FIG. 11. Equilibrium diagram of the iron-zinc alloy system.

such as is used for sheets and wire. The iron content of the bath, at least in the upper portion, in the latter case usually is not very different from the saturation value for the solution of iron in molten zinc at the bath temperature used.

The accumulation of the dross gradually interferes with the operation of the bath so that it has to be removed periodically, usually once a week. The material removed consists of a zinc-rich matrix, embedded in which are the crystals of the iron-zinc compound. The average iron content of the dross or "hard zinc" as it is often called is very considerably below that of the compound $FeZn_7$. According to Altpeter [B 11] 2 to 3 per cent of iron is the rule. Figure 12 shows the microstructure of some dross which gave the following results on analysis: copper, 0.05 per cent; lead, 3.3 per cent; iron, 3.0 per cent; aluminum, not detected. The presence of the lead is to be explained by its having been entrapped as the dross was baled out from the bottom of the zinc bath.

Open-hearth iron has been recommended as a material having relatively high resistance to the alloying action of the molten zinc. Jones [B 112], however, has published data indicating that the difference in the rate of attack of open-hearth iron, wrought iron (Norway iron) and low-carbon steel is not very appreciable, the relative attack of the three being represented on a scale, arbitrarily chosen, by the numbers 13, 16, and 16, whereas the attack of carbon tool steel (1.00% C) was very much greater, being represented by 348 on the same scale. The observation by Jones, that certain streaks in the low-carbon steels were attacked much more vigorously than the steel as a whole, would suggest that open-hearth iron may be somewhat superior since this material is quite free from such streaks. Diegel [B 50, B 58] has stated that the rate of solution of iron in zinc is decreased somewhat by silicon in the iron but that carbon and manganese do not influence it, at least in the amounts ordinarily encountered in structural steels. Camp and Francis [B 95] state that low-carbon basic open-hearth steel is used very widely. Sang [B 48] has recommended nickel steel as being very resistant to the action of the molten zinc. The results of commercial practice have not shown any decided superiority for this material, however.

Addition of aluminum.—The addition of a small percentage of aluminum to the molten zinc, first proposed by Joseph Richards, is favored by many. The aluminum is not added as the metal, but in the form of a zinc-aluminum alloy, known under various trade names, the composition of which is not fixed but generally contains considerably more than 10 per cent aluminum. The amount of aluminum in the bath, and hence in the coating, naturally varies with the operator of the plant. An addition of 0.05 per cent produces a noticeable effect and with 0.25 per cent aluminum the effect is very marked.

The aluminum treatment is not generally favored in the coating of

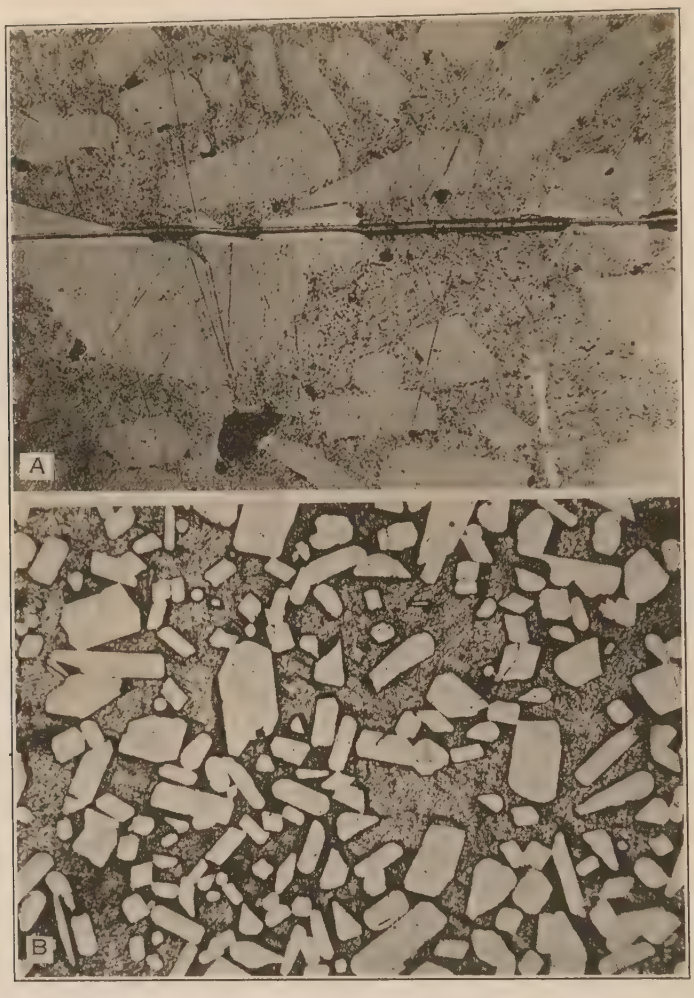

FIG. 12. Microstructure of the iron-zinc alloy, "dross," which collects at the bottom of the molten zinc bath used in galvanizing. This material contained 3.3 per cent iron. × 250.

A, unetched. The scratch shows that the crystals, which contain considerable iron, are much harder than the zinc-rich matrix in which they are embedded.

B, same alloy etched. Etchant, 100 cc. water, 20 gm. chromic acid, 1.5 gm. sodium sulfate.

sheets in the United States. Aluminum treatment is most widely used in the hand-dipping process for irregularly shaped articles, especially products fabricated from sheet metal, such as pails, tubs, vats, and the like, as well as bolts, nuts and anything having rather sharp crevices. The greatly increased fluidity of the aluminum-treated bath is a decided

advantage in coating such articles since the zinc must penetrate all crevices and in the case of fabricated articles, such as buckets, it must function as a solder as well as a protective coating. The coating as a rule is thinner than one from an untreated bath but much more uniform in thickness and with a whiter appearance. The action of the aluminum has not been clearly established but it has been attributed to its deoxidizing action on mechanically entrapped zinc oxide in the molten bath [B 48]. It has been stated also to have some effect upon the alloying of the zinc and iron. Figure 13*a* shows the structure of a zinc

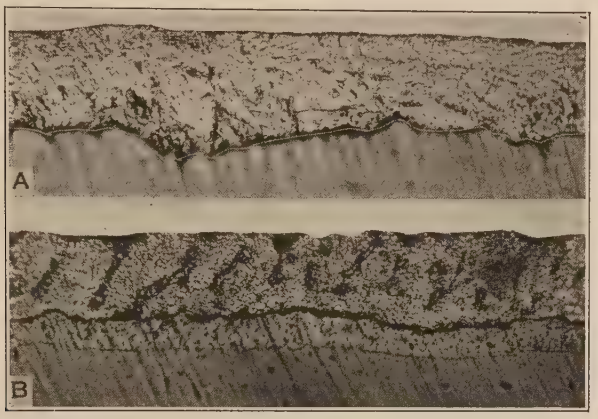

FIG. 13. Effect of additions to the zinc bath on the structure of the coating. × 350. [B 121]. Etched as in Fig. 8.

A, The bath was treated with 0.2 per cent aluminum. Note the absence of alloy layers; compare Fig. 16.

B, The bath was treated with tin. The oblique markings in the outer, or zinc-rich layer of the coating are the patches of tin-zinc eutectic.

coating produced by the dipping process, the bath having been treated with 0.2 per cent aluminum. The absence of the alloy layer is very evident.

Figure 14 shows how an increase in the aluminum content of the zinc bath results in a decreased thickness of coating. Bablik [B 83] has recommended 0.6 per cent as the optimum aluminum content for use in galvanizing. It is somewhat doubtful, however, whether a zinc coating with such a high aluminum content would prove satisfactory in service, especially in warm moist climates. The well-known tendency of zinc-aluminum die-casting alloys containing small amounts of impurities such as lead, cadmium or tin to disintegrate by intercrystalline corrosion [B 141] under such conditions suggests that zinc coatings containing aluminum in the amount recommended might also disintegrate in a similar manner. One difficulty in the use of aluminum in galvan-

izing which must be guarded against is the effect upon the ammonium chloride flux. On account of the flux being rendered less fusible, the surface of the coating may have a rough inferior appearance as a result.

Addition of tin.—Tin is sometimes added to the zinc bath to improve the surface appearance, and to ensure uniformity of coating thickness [B 95]. Amounts as high as 3 per cent have been reported.

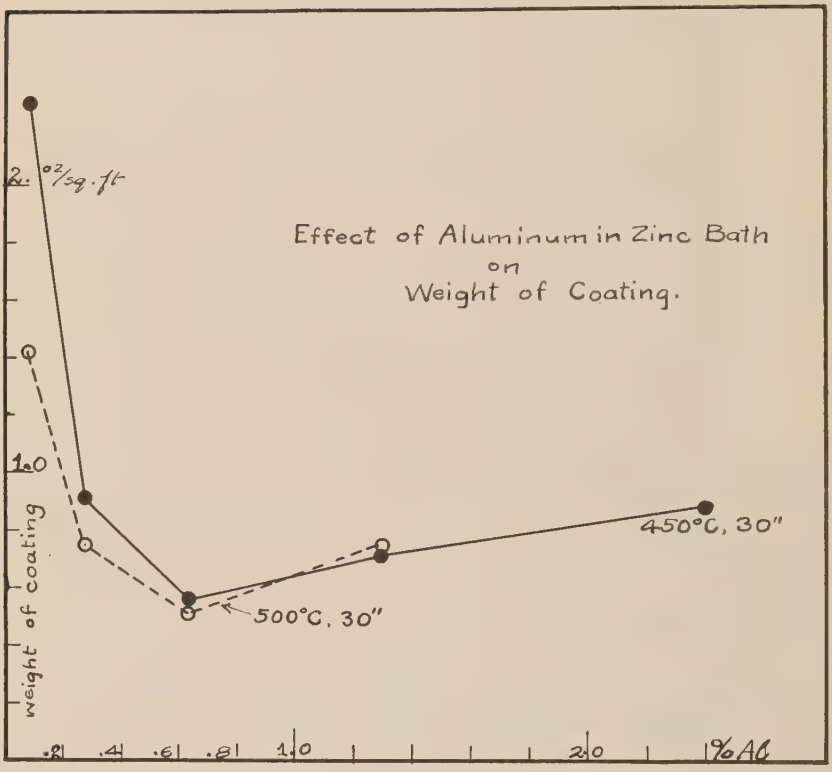

Fig. 14. Effect of aluminum in the zinc bath on the weight of coating [B 83].

The usual amount is considerably below 1 per cent, however. The surface of such coatings is said to tarnish rather easily. The effect of tin on the zinc-dipping process is, in all probability, to be ascribed to its influence on the melting point of zinc as shown in Figure 15. The addition of even small amounts causes the freezing of the metal to be spread over a considerable range of temperature, solidification not being complete until a temperature of 198° C. (388° F.) has been reached. Figure 13*b* shows the structure of a zinc coating containing tin. The diagonal markings in the outer or zinc-rich layer of the coat show how

the tin, in the form of the tin-zinc eutectic, is distributed throughout the coating.

The results summarized in Table 3 show the composition of the coating on five different commercial zinc-coated sheets of American manufacture. According to these results, none of the manufacturers had used aluminum but all the coatings contained nearly the same amount of lead. Tin had evidently been used intentionally by at least three of the five.

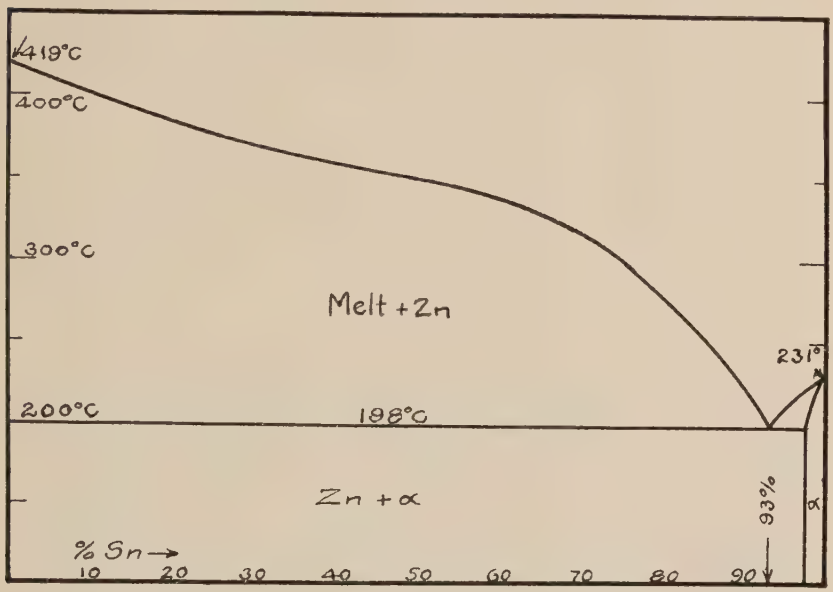

FIG. 15. Equilibrium diagram of the tin-zinc series of alloys.

The temperature of the bath.—The melting point of zinc, as reported by the Bureau of Standards, is 419.4° C. (786.9° F.). Obviously the bath of molten zinc must be kept at a temperature somewhat higher than this. The average working temperature usually regarded as suitable in coating sheets is 450° C. (840° F.). Finkelday [B 94] has reported 445-465° C. (830-870° F.) as the average temperature used in zinc-coating wire. The alloying action of the molten zinc on iron is accentuated by an increase in temperature. A kettle should last from 10 to 18 months if given proper care [B 95]; Diegel [B 62] states that the most common cause for the very short life of the pots used is the fact that a working temperature of 500° F. or so is used instead of one 50 degrees (C.) lower. The results obtained by him for different samples of sheet steel immersed in molten zinc show very

TABLE 3.—COMPOSITION OF COMMERCIAL HOT-DIPPED ZINC COATINGS ON SHEET IRON AND STEEL.[1]

Sample	Weight of Coating	Composition					
		Fe	Sn	Pb	Cu	Sb and Al	Zn[2]
	Oz./sq. ft.	Per Cent					
A	1.77 1.81 1.78	3.7	0.10	0.80	0.09	n.d.[3]	95.31
B	2.95 2.64 2.27	3.5	.70	.72	.06	"	95.02
C	1.81 2.60 2.28	3.2	.22	.71	.05	"	95.82
D	1.48 1.08 1.22	2.7	.08	.82	.02	"	96.38
E	2.57 2.68 2.41	3.1	.73	.81	.02	"	95.34

[1] Sheets of regular commercial grade.
[2] By difference.
[3] Not detected.

clearly (Table 4) the pronounced increase in the rate at which iron is dissolved by zinc as the temperature is increased. The lower loss obtained with the high carbon steel is not consistent with the established fact that cast iron is attacked by molten zinc so much more rapidly than low carbon steel that it is impracticable to use cast iron gears on machines for zinc-coating sheets. Instead, the gears are cut out of wrought iron or low carbon steel. The results reported by Jones [B 112] also do not agree with those of Diegel with respect to the relative losses of high-carbon and low-carbon steels when immersed in molten zinc.

TABLE 4.—EFFECT OF TEMPERATURE ON THE RATE AT WHICH IRON IS DISSOLVED BY MOLTEN ZINC [B 62].

Steel Specimen	Loss in Grams per Hour per Square Meter				
	450° C.	475° C.	490° C.	500° C.	524° C.
A(0.11% C)	22.0	27.8	30.6	89.0	347.6
D(0.10% C)	21.6	27.8	31.0	134.9	339.0
E(0.11% C)	22.3	27.8	32.6	289.3	379.7
F(0.12% C)	24.7	26.9	32.2	282.7	804.6
B(0.30% C)	292.6(?)	31.4	148.2	209.0	168.9
C(0.80% C)	20.1	25.5	30.4	46.1	58.7

For large heavy objects in which the surface area is relatively small as compared to the mass of the body a somewhat lower temperature than for smaller ones is advisable; for example, Touceda [B 54] rec-

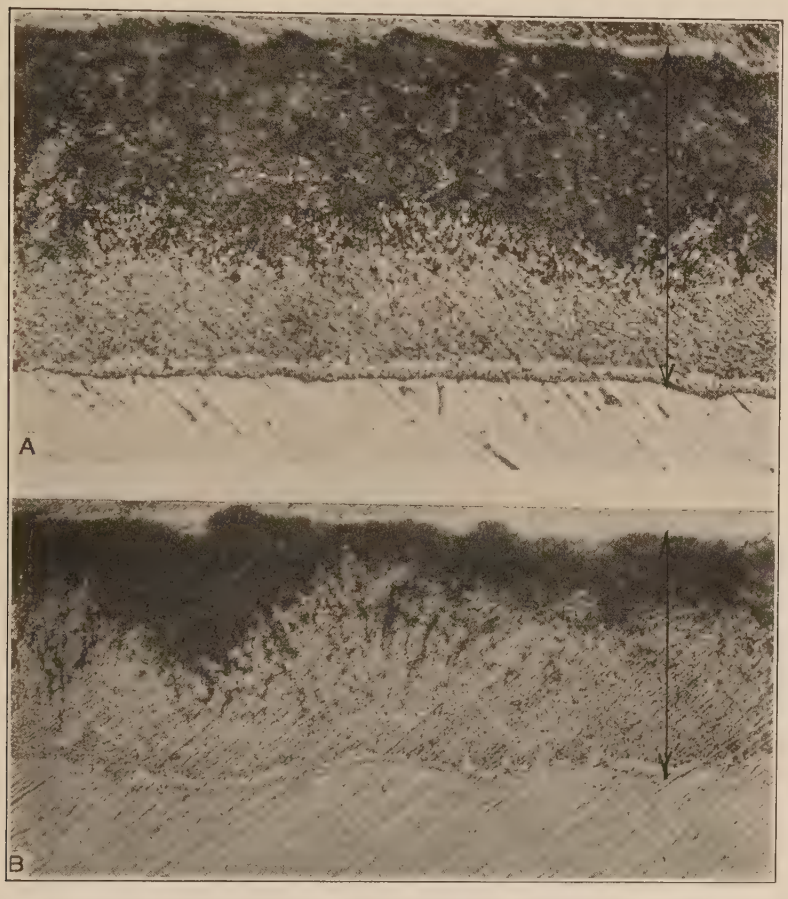

FIG. 16. Structure of zinc coatings on steel produced under unusual conditions, × 500 [B 113].

A, The coating machine was stopped and the sheet was held in the bath for 2 minutes.

B, A sheet was run through the molten zinc bath four times.

Note the well developed alloy layers (light-colored portion of the coating) adjacent to the steel base. The arrow indicates the total thickness of the coating. Etchant, 1 per cent alcoholic solution of iodine.

ommends 425° C. (800° F.) for the zinc coating of large malleable castings and 475° C. (890° F.) for small ones. Since it is necessary in any case that the articles attain the temperature of the bath in order for adherent coatings to form, the large pieces must remain in the zinc

considerably longer than small ones. The tendency is for increased alloying action in the coatings as the period of immersion is increased, temperature remaining constant, hence the reason for a somewhat lower coating temperature recommended for the heavier pieces. Figure 16 shows two sheets held in the zinc bath for different periods. Although the coating thickness did not vary in the same ratio as the immersion periods, the amount of alloy formation in the one held for the longer time was much more marked than in the other. The results shown

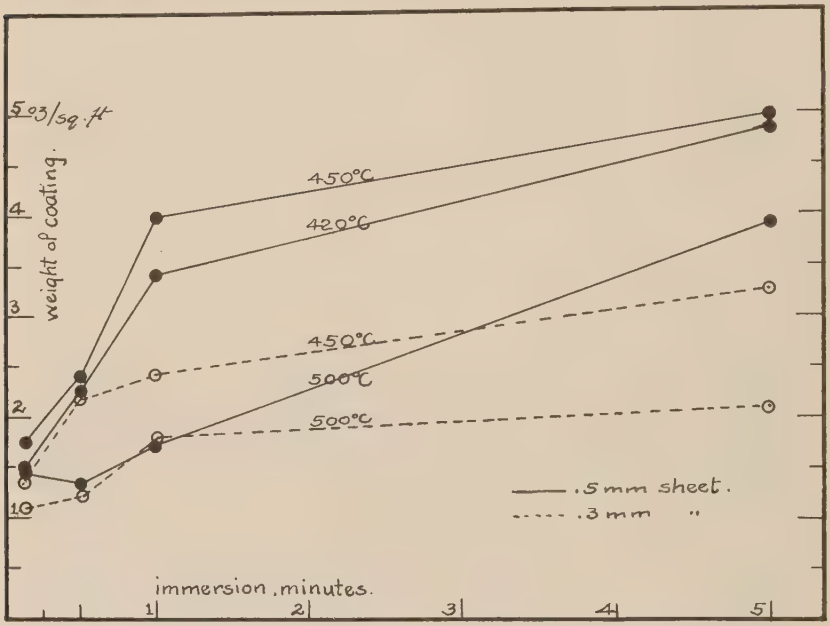

FIG. 17. Effect of length of immersion period at various bath temperatures on the weight of the zinc coating [B 83].

in Figure 17 are from data given by Bablik [B 83] showing the variations obtained in the thickness of zinc coatings made on a laboratory scale as the immersion period and temperature of the bath were varied.

The flux.—That portion of the surface of the metal bath through which the article is passed into the molten metal is kept covered with a flux. In hand-dipping installations a transverse partition across the upper part of the bath extending a distance of about 3 inches below the surface of the molten zinc prevents the molten flux from spreading over the entire surface of the bath. Ammonium chloride is the flux in widest use for zinc. A small amount of crude glycerin was formerly considered very necessary. Tallow is used considerably at present.

The mixing of the ammonium chloride or "sally" flux is an operation requiring a good deal of experience and there is very little information in the technical literature on the subject. Bablik [B 88] has reported some work along this line but on the whole the subject is a very obscure one. Camp and Francis [B 95] believe that the prime function of the flux in galvanizing is to ensure a dry surface before the metal passes into the molten zinc.

The flux also prevents the formation of oxide on the surface of the molten zinc which would stick to the surface of the article to be coated and either give a very rough coating or prevent complete adherence of the coat to the base. The flux also without doubt serves, just as in the soldering operation, to clean the metal at the instant it strikes the molten bath.

In the zinc-coating of wire, the use of zinc chloride solution as a flux bath, outside of the pot, is favored. The wire is dried after passing through the solution and then passes on into the zinc. The adhering film of zinc chloride prevents any oxidation during drying. There is also a tendency on the part of some operators toward the use of zinc chloride in the galvanizing, by hand dipping, of large structural steel members.

At the exit end of the metal bath, a flux covering is not used, except in some very special cases. In the hand-dipping process, the surface is cleaned off with a wooden spatula just before the article is brought out. At the most, only very slight oxidation occurs which has no effect upon the wearing properties of the coating although it may alter the appearance somewhat. It is claimed [B 48] that, with an aluminum-treated bath the tendency for surface oxidation is much reduced. After hand dipping, the coated article, such as a tub, is turned upside down to allow all excess zinc to drain off and may also be rapped sharply to aid in removing the excess zinc. Machines have been devised for removing the excess zinc from small articles, bolts, nuts, nails, small castings and the like, by shaking [B 42] or by a centrifuge [B 63].

Most zinc-coated wire, except that known as telegraph wire, is "wiped" as it emerges from the molten zinc to remove excess zinc and to give a smooth surface. The wiper may be a pad of asbestos which can be held on the opposite sides of the wire by suitable adjustable steel clamps. Telegraph wire is not wiped and hence has a somewhat rougher appearance than fence wire. In the latter case if the wiping is very severe only a very thin coating remains, which may consist almost entirely of the zinc-iron alloy layer. This is shown in Figure 18 which also shows the effect of bending upon coatings of this kind. The wiping of wires during galvanizing is not simply for the purpose

of saving zinc, as is often supposed, but is often necessary in order to produce a coating which will withstand rather severe bending.

For making wire with exceptionally heavy coating, the wiping may be done by drawing the wire vertically from the bath through a "header" of sand, charcoal or fine cinders [B 95]. A hollow cone of zinc quickly freezes around the wire and functions as the wiper. Finkeldey [B 94] has described how wire with an exceptionally heavy zinc coating

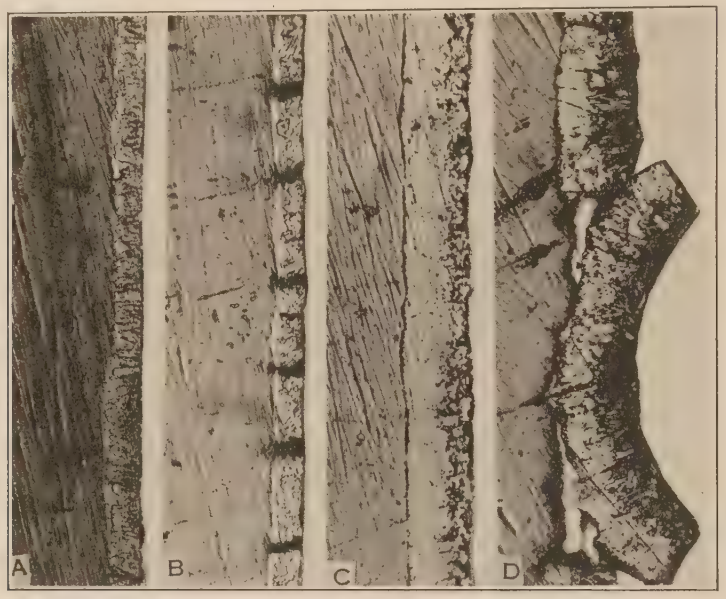

FIG. 18. Structure of the zinc coating on "wiped" wire, × 350. [B 121.] Etched as in Fig. 12.

A, "tight wiped" wire. All of the coating except the alloy layer has been wiped off.

B, same as *"A"* after the bend test in which it was wrapped around a wire of the same diameter.

C, "asbestos-wiped" wire. The coating was not so closely wiped as in *"A."*

D, same as "C," after the bend test of *"B."* The rough uneven surface of the alloy layer is largely responsible for the flaking upon bending.

such as is required for the construction of cables for suspension bridges has been successfully made in this manner. The pickled wire, carefully washed free from iron salts, after passing through the flux bath (25% $ZnCl_2$ solution, acidified with HCl) was passed through a bath of high-grade cadmium-free zinc, at a temperature of 445° to 465° C. (820-870° F.). Five to seven seconds was required for any point of a wire of No. 12 gage to traverse the zinc bath. For a larger wire, No. 6 gage, such as was used on the Delaware River

Bridge, 17 to 20 seconds' immersion in the zinc was required. The wire was drawn vertically from the bath through a 4 or 5 inch layer of granular charcoal saturated with tallow and carried vertically for a

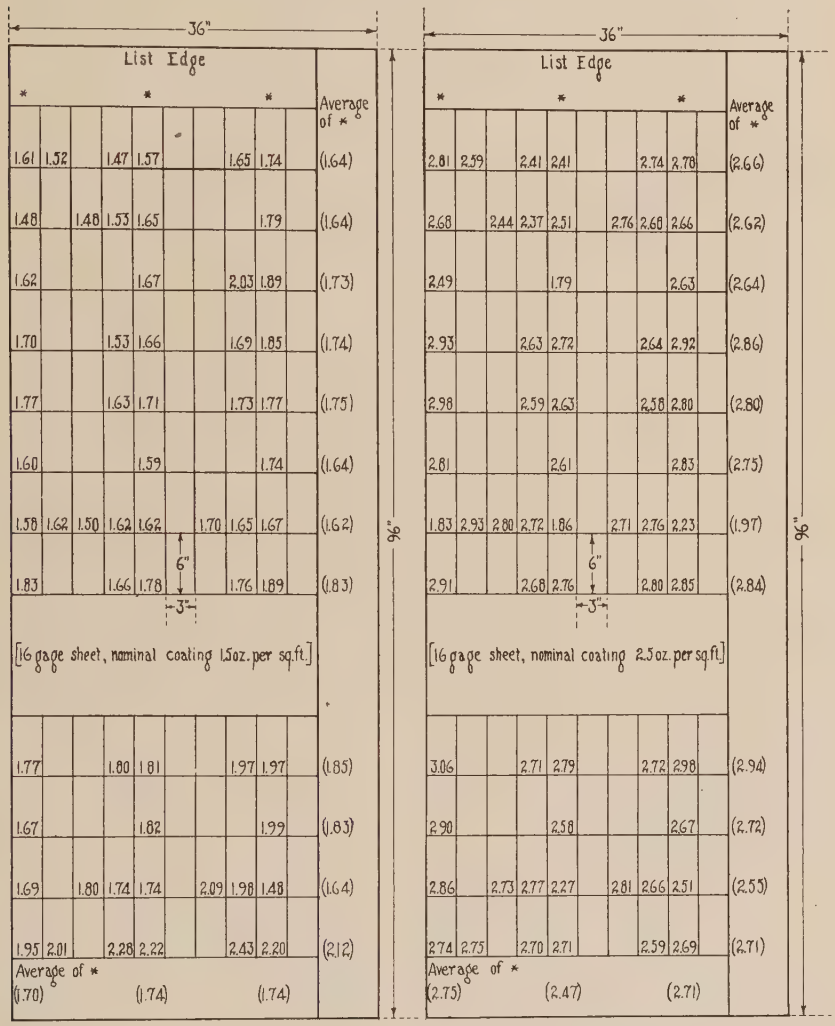

FIG. 19A FIG. 19B

FIG. 19. Variations in the thickness of the zinc coating on galvanized sheet [M 35].

distance sufficient to permit solidification to occur before the wire reached the first pulley. With a zinc chloride flux bath the period of immersion in the zinc was approximately only one-fourth as long as was necessary with a hydrochloric acid flux bath.

In the coating of sheets by machinery, the thickness of the coating can be regulated, at least approximately, by the setting of the exit rolls (Fig. 9) with respect to the surface of the zinc bath. By slightly changing the position of the rolls (often by adding more zinc to the bath), so as to increase the amount of zinc in the V-groove between the two rolls, a thicker coating results, other conditions of operation remaining the same. The thickness of the coating on sheets varies somewhat from sheet to sheet and may vary rather widely on different portions of the same sheet. A variation of 17.5 per cent, that is, a variation of 0.35 ounce per square foot in a nominal coating of 2 ounces per square foot, is considered by many manufacturers [B 95] as good commercial practice even with the present-day equipment. Figure 19 (*a* and *b*) shows the variations in thickness of coating found on two sheets representative of a total of 47 which were surveyed for variations of coating thickness in the manner shown [M 35]. The results of the investigation did not reveal any pronounced systematic variation in the thickness of coating on galvanized sheets.

As a general rule no flux coating is used at the exit end of the bath. For some special cases such a coating is employed. Poppleton [B 65] has described a special type of English-made sheets coated by zinc dipping in which a flux of ammonium chloride, tallow and glycerine (slightly less than 3 per cent of each of the two latter) was used on the sheet as it left the molten zinc. It was referred to as a high grade product and other special precautions were taken in its manufacture. A patented process, known commercially as "flux finishing" [B 56], is claimed [B 95] to give a much more uniform coat on a sheet than can be obtained by the ordinary method of coating. A powdered flux is blown upon the "feed-out" rolls of the zinc-coating machine and onto the surface of the molten zinc as the material which is being coated emerges from the bath of metal.

Effect of Impurities in the Bath.

The use of high grade zinc for the bath in the hot-dipping process has been frequently advocated. It is the usual opinion of the practical man engaged in this work that virgin metal is far superior to zinc reclaimed from dross or other sources and that zinc of very high purity is not so desirable as one containing appreciable amounts of certain other metals.

Unquestionably, some of the impurities with which commercial zinc may be contaminated are detrimental in the operation of the hot-dipping process. However, the reasons for some of the recommendations which have been made concerning the purity of zinc are not apparent.

Iron, lead, aluminum, and cadmium have been listed [B 16] as very undesirable in zinc which is to be used for the hot-dipping process for certain products for which relatively heavy ductile coatings are required, although for ordinary practice they need not necessarily cause much concern.

Since the hot-dipping process as carried out commercially at present always requires the use of a steel or iron container from which, if from no other source, the zinc becomes saturated with iron in very short order, a warning against this impurity, at least in small amounts, is unwarranted. American Society for Testing Materials Standards B 6-18 [B 87] permit 0.08 per cent of iron in "prime western" zinc, which is the grade generally employed commercially for zinc coating by hot dipping.

Lead is often added to the zinc bath intentionally, as stated above, particularly if the zinc used is low in this element. The same specification, B 6-18, permits a lead content of 1.60 per cent in the prime western grade of zinc. At a temperature just above the melting point of zinc (419° C.) molten zinc can hold approximately 1 per cent of lead in solution [B 99, B 100] (*See* Fig. 11). The solubility increases somewhat with increase in temperature, being approximately 2 per cent at 475° C. (885° F.). Any excess above this amount, therefore, gradually collects in the bottom of the bath as a separate layer. Lead is added to increase the depth of this layer if the amount in the zinc used is low, that is, much below the solubility limit shown by the zinc-lead equilibrium diagram.

In addition to the effect which lead seems to have upon the formation of the spangle which the trade demands in galvanized coatings and the advantage of having a lead layer to aid in the "dedrossing" operation, it is the firm opinion of most practical men that a certain amount of lead is advantageous to the hot-dipping operation, *per se*. Smooth and uniform coatings with a well developed spangle can be obtained more easily if lead is present than if a higher grade zinc is used. No satisfactory reason for this has been advanced. On the other hand, the claim has been made that zinc coatings with large spangles have been produced experimentally with lead-free zinc [B 118, *discuss.*].

Hannah and Rhead [B 118], in their laboratory study of the cause of the gray appearance of certain zinc-dipped sheets concluded from the results of corrosion tests in acid that coatings containing lead are not so resistant as those without lead. Arguelles [B 134] has reported zinc coatings which stood up satisfactorily in service in a tropical country for 30 years. Some of these coatings he referred to had a lead

content of 0.5 to 0.8 per cent and an iron content of 2.8 to 5.3 per cent. The conclusion is obvious; for this particular type of atmospheric exposure, neither lead nor iron in the amounts stated can be considered as having had any very pronounced detrimental effect upon the corrosion resistance.

Tin is another metal frequently added to the zinc bath. No convincing evidence has been published which would indicate that its use is undesirable from the standpoint of corrosion resistance, although Sang [B 48] states that, on account of the difference in the electrolytic solution potentials of tin and zinc, the corrosion resistance of zinc coatings containing tin would be expected to be inferior to those without this metal.

There has been considerable discussion concerning the detrimental effect of cadmium. Its absence in zinc is claimed [B 14, B 16] to be necessary for the coating of very high grade products such as telegraph and telephone wire, which must be heavily coated and still be capable of withstanding severe deformation. Very high grade zinc has been used also in coating the wire used in such important constructions as suspension bridges. According to Trewin [B 92] and Finkeldey [B 94] the zinc coating of the wire in the cables of both the Delaware River Bridge at Philadelphia and the Hudson River Bridge at Bear Mountain is of this character.

Aluminum treatment of the zinc bath is a common practice, and like the corresponding practice in steel manufacture its usage is perhaps more widespread than is generally supposed. According to Primrose [B 118, *discuss.*] the presence of very small amounts of antimony in the zinc bath will suppress the spangle effect even in the presence of considerable amounts of lead. It is claimed that this assists very materially in permitting the coatings to withstand flexure without peeling. The same is said for aluminum also. The absence of a well developed alloy layer in coatings made from aluminum-treated zinc baths (Fig. 12*a*) tends to confirm this statement.

In any consideration of the effect of impurities upon the service life of the zinc coatings in which such impurities occur, the structure of such coatings must be borne in mind. For most practical purposes, a hot-dipped zinc coating may be looked upon as made up of two layers which differ markedly in their composition and properties, the underlying alloy layer and the surface layer of relatively pure zinc. Observations on the effect of impurities on the corrodibility of zinc may be considered as having some bearing on the behavior of the outer layer but very little, if any, direct bearing on that of the alloy layer which, as the outer one is corroded away, becomes the exposed surface.

Prost has studied the effect of impurities in sheet zinc upon the rate of corrosion of such material in dilute acids as well as under atmospheric corrosion. He concluded [B 137] that the presence of small amounts of lead, iron or cadmium, which are common impurities in commercial rolled zinc as made in Belgium, increases the corrosive attack of zinc by dilute sulfuric acid and by dilute hydrochloric acid. The addition of antimony, arsenic, copper, or tin, even in very small amounts, to zinc containing the first three impurities serves to increase very appreciably the rate of attack by the acid.

From the results of atmospheric corrosion tests of the same materials carried out over a period of five years, 1914 to 1919, he decided that antimony and copper were the only two common impurities whose effect was at all strongly marked. Antimony in amounts from 0.03 to 0.07 per cent seemed to have an accelerating effect, whereas small amounts of copper, even a few hundredths of one per cent, appeared to exert a protective action. Variations in the cadmium, lead, or iron content had no appreciable effect upon the corrodibility of the sheet zinc used, the average composition of which was: lead 1.12 per cent, cadmium 0.10 per cent and iron 0.03 per cent. The presence of small amounts of tin (0.005%) or arsenic (0.09%) did not influence the rate of atmospheric corrosion.

The results recently obtained by Vondrácek [B 147a] on the influence of impurities in zinc upon its solubility in acids confirm those of Prost, with the exception of lead. Vondrácek reports that both mercury and aluminum when present in zinc have a decidedly lowering effect upon its rate of solution in dilute sulphuric acid. Lead has an almost entirely negligible effect whereas all the other metals used, when present as impurities in zinc, increase its rate of solution in sulphuric acid in the following order: cadmium, arsenic, tin, antimony, iron, copper. No exposure tests were made, however, to correlate the results of these laboratory tests with the behavior under service conditions of the same materials.

The influence of impurities in a zinc coating upon the corrosion-resistance of the coating is of relatively minor importance as compared with the thickness of the coating. The limitation in the maximum thickness, in the case of sheet and wire, is dependent in large measure upon the severity of the mechanical deformation which such materials may have to withstand when fabricated. The American Zinc Institute, through its Committee on Galvanizing [B 147], has recently recommended a 2-ounce coating on galvanized sheets, that is, 1 ounce per square foot on each side, as the best "all around" coating for this class of material.

The general subject of specifications for zinc-coated materials has recently received a good deal of attention, and the organization by the American Engineering Standards Committee of a Sectional Committee on Zinc Coating of Iron and Steel for working on this subject marks a distinct advance. The various zinc-coated commercial products for which specifications are needed have been classified by this sectional committee under the following headings: hardware and fastenings; sheets and sheet products; plates, bars, structural shapes and their products; pipes, conduits and their fittings; wire and wire products.

Defects in Zinc Coatings.

The defects looked for in the inspection of zinc-coated sheets may be taken to illustrate in general the defects which may occur in coatings made by the dipping process. Defects of a mechanical origin bearing no definite relation to the hot-dipping coating method as such, need not be considered; the following, however, are intimately related to the method of coating.

Adhering spots of the black or dark-colored flux, which are sometimes termed "sally spots" in the mill, constitute one type of defect. These are primarily defects in appearance only as it can generally be shown by scraping off the adhering deposit that the sheet is coated with zinc underneath the spots. Such spots are generally scraped off and the sheets passed through the zinc bath again. Incomplete removal of the oxide scale in the first pickling operation usually results in bare or "black spots". Many such sheets can be reclaimed by scraping the spots free from scale, cleaning them with acid and recoating the sheet in the zinc bath.

Not infrequently the sheets after coating have a rough gray appearance, sometimes in certain portions only and at other times over the entire surface. The beautiful fern-like pattern or spangle (Figs. 20 and 21), which the trade regards as very desirable and as characteristic of high grade material may be entirely lacking on such sheets (*See* Fig. 22). This type of defect, the "gray sheet", is not infrequently a cause of serious concern to sheet manufacturers.

Hannah and Rhead [B 118] concluded, as a result of a laboratory investigation of this subject, that the spangle of hot dipped zinc coatings is independent of the nature of the steel sheet used, and is more intimately related to the impurities in the zinc bath. They were unable to secure a good spangle in coatings made with pure (i.e., untreated) zinc, and additions of aluminum and tin in the amounts used in commercial practice did not aid any, which is contrary to what has been claimed by others [B 48, B 95]. However, the presence of lead or

FIG. 20. Zinc-coated sheet showing very large "spangles," natural size [B 114].

FIG. 21. Zinc-coated sheet showing medium size "spangles," natural size [B 114].

bismuth did facilitate very markedly the production of a spangled surface. Qualitative chemical analyses of their zinc-coated specimens showed a very appreciable difference in the lead content according to the size of spangle. The coatings in which the spangle effect was lacking on account of the small crystal size showed a much higher lead content than those having a large spangle.

The results of the investigation, however, do not appear to warrant their first general conclusion. As was pointed out in the discussion of

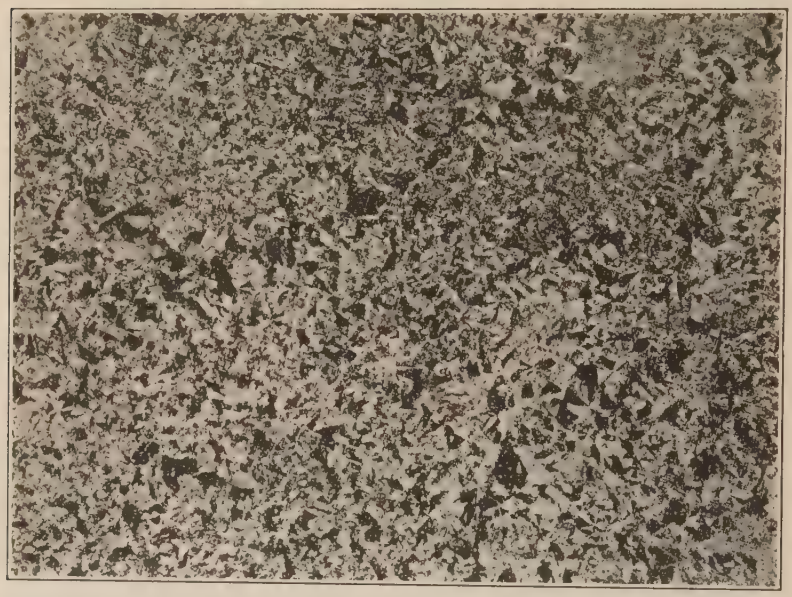

FIG. 22. Zinc-coated sheet, natural size, showing a granular dull appearance, generally known as "gray zinc" [B 114].

the paper and elsewhere [B 114], the results obtained in practice in the coating of sheets by hot dipping will not substantially support such a conclusion.

The statement, backed by numerous observations in the mill, has been repeatedly made [B 65] that over-pickling of a sheet is very apt to cause the gray appearance. White [B 114] has clearly shown that the base metal plays a part in determining the character, at least the appearance, of the zinc coating. He has also shown that with the same zinc bath some sheets will show the gray appearance whereas the majority of those coated at the same time have the spangled surface. Representative gray and spangled sheets when stripped of their coating by dilute acid and passed through the bath a second time give essen-

tially the same results as when first coated. In short, gray sheets persisted in remaining "gray". Similar results were obtained by White with coated sheets which were gray in certain restricted areas only. Such areas, the location of which was permanently marked on the sheet, showed the same gray appearance when the sheet was recoated, after having had the first coat removed. Coated wrought-iron sheets never have the beautiful spangled surface that steel sheets do, their char-

FIG. 23. Zinc-coated sheet similar to that of Fig. 20 after the outer zinc-rich layer of the coating had been removed by means of dilute acid. The surface of the alloy layer is shown, × 10. [B 114.]

acteristic appearance being on the order of gray sheet. However, if a wrought-iron sheet is cleaned mechanically, that is, without pickling in acid, a very marked change results upon coating and the spangle is often well developed.

White concluded from his experimental data that the retention of hydrogen by the iron during the pickling operation is fundamentally responsible for the production of gray-coated sheets. Gray and spangled sheets from which the coating down as far as the alloy layer is removed by means of dilute acid, show a characteristic difference in appearance. The surface of the gray sheets was found to be covered with numerous elevations of "blisters" which were almost entirely lacking in the well spangled sheet, as shown in Figures 23 and 24. The "blisters" were interpreted as being an effect caused by hydrogen evo-

lution during or just after the formation of the alloy layer. The roughened surface thus produced afforded excellent opportunity for numerous crystallization centers and hence for a relatively large number of zinc crystals to form on the surface, whereas on the smoother surface fewer nuclei for crystallization were to be found and larger crystals resulted.

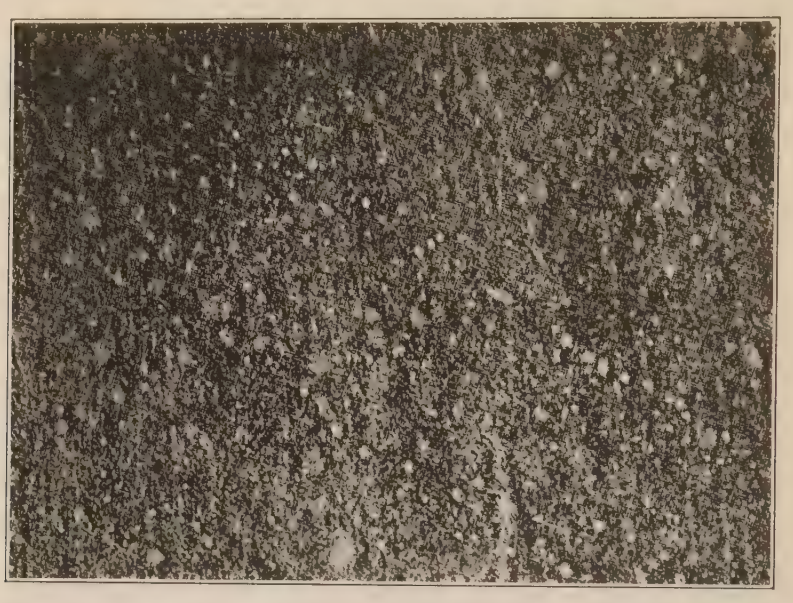

FIG. 24. Zinc-coated sheet similar to that of Fig. 22, the outer zinc-rich layer of the coating having been removed by means of dilute acid. The surface of the alloy layer is shown, ×10. [B 114.]

The retention of hydrogen during the pickling of the steel sheets, according to White's data, is related to the "quality" of the sheet, particularly to the character of the inclusions. The presence of iron oxide, indicative of an insufficient or incomplete deoxidation treatment, was claimed by him to be a common source of the trouble. The rough surface in such sheets resulting from pickling appears to favor the retention of the hydrogen which later gives rise to the gray appearance. Further work along this line is needed to substantiate these conclusions.

It appears, therefore, from the data available that the gray appearance of zinc coatings made by the hot-dipping process is not to be attributed to any single cause. Any condition which favors the production of a great number of crystallization centers on the surface of the sheet, particularly on the surface of the alloy layer, is favorable to the gray appearance. This may be the condition of the surface of the sheet

itself as White has shown, or of the zinc bath as shown by Hannah and Rhead. Substances of slight miscibility in zinc by their separation from the molten bath upon cooling serve as crystallization centers. Quenching a zinc-coated article in water before the zinc has set will also prevent the formation of the spangle.

The demand which has gradually grown up in the trade for a well spangled sheet is based on the appearance rather than the superior quality of such sheets. There is no good evidence that spangle is any indication of quality [B 95]. Singmaster [B 90, 151a] states that some users specify "freedom from spangle" for certain high grade galvanized products and he regards spangle as usually being an indication of a thin coating and as often denoting a somewhat inferior quality. The results obtained with certain accelerated corrosion tests (p. 230) show that on sheets having large and well developed spangles the outer or zinc-rich layer of the coating is relatively very thin along the margins of the individual spangles. As the outer layer coating is slowly and progressively stripped off by such a test, the underlying alloy layer is exposed along the margins of and in between the adjacent spangles relatively early in the course of the test.

Blisters in galvanized sheets are practically always associated with defects of the steel base rather than with the coating. Lindemuth [B 150a] has recently suggested that the formation of blisters in this type of material is to be associated with the presence of moisture which has been taken up by the sheets and retained in discontinuities in the metal, in the interval between the pickling and the zinc-coating operations. It is claimed by him that the tendency toward blistering can be very greatly reduced by thoroughly drying the sheets just before they are immersed in the zinc bath. On the whole, however, blistering is not a very common defect on zinc-coated sheets.

The Microstructure of Iron-zinc Alloys.

The pronounced solvent attack of molten zinc on iron or steel in contact with it has been repeatedly referred to in the foregoing discussion of the process of zinc coating by hot dipping. As a consequence of the alloying action between the two metals, the coating produced by hot dipping is far from being simply a layer of zinc spread over the surface of the steel. According to Peirce [B 117] an iron content of only a few hundredths of a per cent is required in order to affect the structure of zinc to such an extent as to render the change detectable under the microscope.

Figure 11 shows a portion of the equilibrium or structural diagram of the zinc-iron system of alloys. Considerable difficulty is involved

in preparing zinc-iron alloys of a very high iron content on account of the loss of zinc by volatilization at the high temperature necessary, so that the entire diagram has not yet been established with certainty. The portion of the diagram relating to the zinc-rich alloys is fairly well understood, however, and so far as the consideration of zinc coatings is concerned is sufficiently accurate for the purpose. The diagram given in Figure 11 is based largely upon the work of Von Vegesack [B 102] and of Raydt and Tammann [B 109] as modified by Peirce [B 117]. Wolgodine [B 101] also contributed to the earlier studies of this alloy system.

Only a very small amount of iron can exist in solid solution in zinc. The redetermination of the limit of solid solubility constitutes the main contribution of Peirce to the diagram. As a result of microscopic studies and the determination of the electrical conductivity, Peirce placed the limit of solubility at 0.02 per cent iron. Von Vegesack as well as Raydt and Tammann previously had set the value at approximately 0.7 per cent iron. It should be pointed out that the validity of Peirce's modification depends somewhat on the assumption that no change in solid solubility occurs as the temperature of the alloy is raised. It is not unlikely, however, that the solid solubility of iron in zinc increases slightly with temperature but still remains very considerably lower than the value given by the earlier workers.

Two intermetallic compounds of zinc and iron of the composition indicated by the formulas $FeZn_7$ (10.9% iron) and $FeZn_3$ (22.16% iron) are shown in the diagram. It is to the presence of these compounds, or at least one of them, that the departure of a zinc-dipped coating from pure zinc, in structure and properties, is to be attributed in large measure. The entire time elapsing during the hot dipping of a sheet, for example, from the immersion of the sheet in the molten zinc until the adhering metal coating solidifies after leaving the bath, is very short, usually only a fraction of a minute. The speed of a sheet passing through the coating machine is from 40 to 70 feet per minute, according to the thickness of coating desired and the thickness of the sheet used [B 95]. Hence, conditions of complete equilibrium such as are implied in the diagram do not obtain in practice. The alloying action is very rapid, however. Finkeldey has shown [B 121] that in the galvanizing of wire, if the iron wire is in contact with molten zinc for so short a period as one-twentieth of a second, an alloy layer can be detected in the microstructure of the coating.

The diagram is very useful in indicating the trend of the changes which may occur, although perhaps not their true magnitude. The

structural conditions in zinc coatings which have been annealed subsequently to the coating operation (Fig. 27) correspond much better to the equilibrium conditions upon which the diagram is based, than ordinary coatings do. Iron-zinc compounds other than those indicated in the diagram have been reported in the zinc-rich alloys [B 94, B 173], the one represented by the formula $FeZn_{10}$ (7.8% iron) corresponds approximately to the upper (zinc-rich) limit of the field *n* of the diagram. The results obtained by Lehmann [B 116] from a study of the magnetic properties of zinc-iron alloys showed a *very* pronounced maximum in the magnetic susceptibility-composition curve corresponding to an iron content of 7.3 per cent. His work was not carried far enough, however (an iron content of 9 per cent being the highest one used), to throw very much light on the constitution of these alloys. Lehmann concluded that the structural diagram of these alloys is probably not so simple as the results of thermal analysis would indicate. It is generally considered that the existence of a definite compound of the composition, $FeZn_{10}$, has not been definitely established. The method described by Storey [B 94] for the preparation of this compound (i.e., separating the crystals in zinc "dross" from the zinc-rich matrix in which they are embedded by dissolving the matrix in dilute acid, collecting the undissolved crystals and remelting them) has not proved successful in experiments carried out by the author. Zinc dross milled rather fine so as to aid in its solution by acid was found to dissolve practically completely in a 5 per cent aqueous solution of hydrochloric acid (by volume). Somewhat better results might perhaps be obtained by dissolving the matrix by a carefully controlled electrolytic method.

Interpretation of the Equilibrium Diagram.

The equilibrium diagram (Fig. 11) is to be interpreted as follows:— as iron is added to zinc and the iron content increases beyond that of the solubility limit, a duplex structure results consisting of crystals approximating in composition $FeZn_{10}$ embedded in a matrix which is the saturated solution of iron (0.02% Fe) in zinc. The second or precipitated phase increases in amount with increase of iron content, until at 7.8 per cent (by weight) this phase constitutes the entire structure of the alloy. As the iron content is increased beyond this amount the composition changes gradually and approaches that indicated by the formula $FeZn_7$ (10.9% Fe). The structure still appears as a single phase (constituent *n* of the diagram) and has many of the characteristics of an intermetallic compound. With further increase in the iron

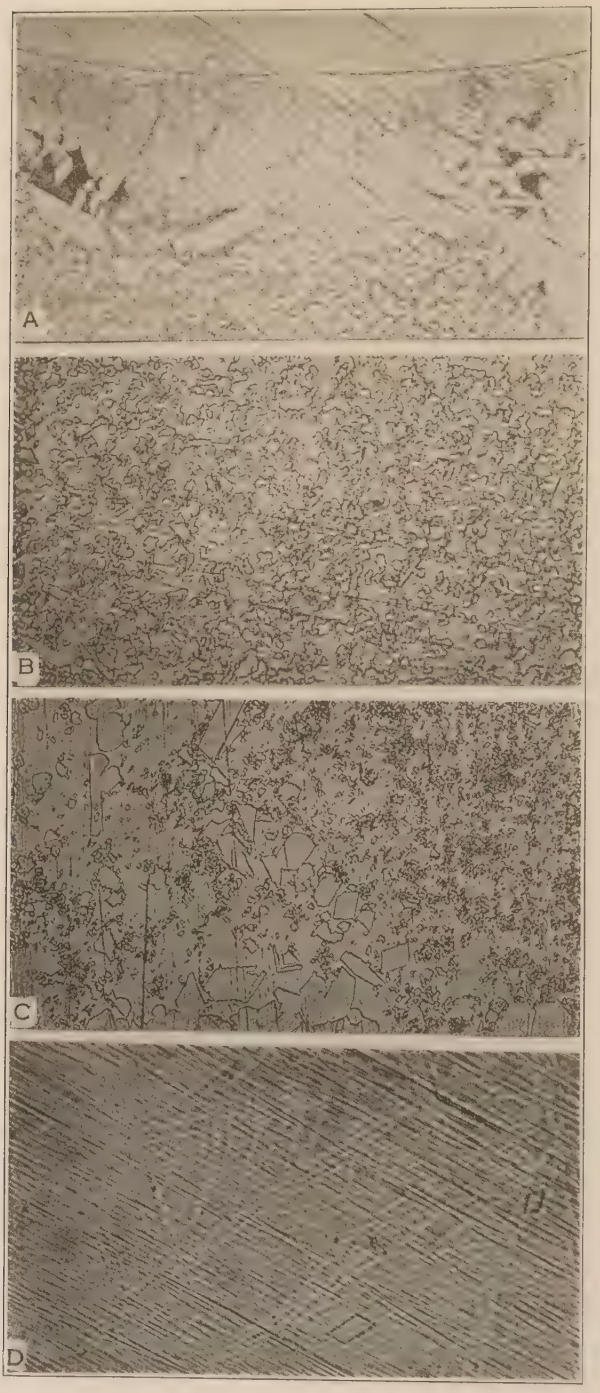

FIG. 25.

FIG. 25. Microstructure of zinc to which iron has been added in increasing amounts [B 113]. An iron wire was held in a small volume of molten zinc, 1 cm^2 cross section, for 4 hours and then the zinc was allowed to solidify around it.

A, Adjacent to the iron wire two distinct alloy layers can be seen; the inner one, presumably $FeZn_3$ is relatively very thin and limited in amount. Crystals of $FeZn_7$ predominate in the outer alloy layer.

B and *C*, Structure typical of the greater part of the zinc outside of the well crystallized alloy layer in *A*. The structure throughout the body of the coating consists of a relatively soft zinc-rich matrix embedded in which are harder particles of an iron bearing constituent. *C* shows the condition somewhat nearer the outer surface than *B*.

D, Outer surface of the coating, some traces of iron (crystals) are to be seen. The shadow-like pattern is rather characteristic of cast zinc.

Magnification; *A*, *B*, *C*, × 500; *D*, × 200. Etchant, 1 per cent alcoholic solution of iodine.

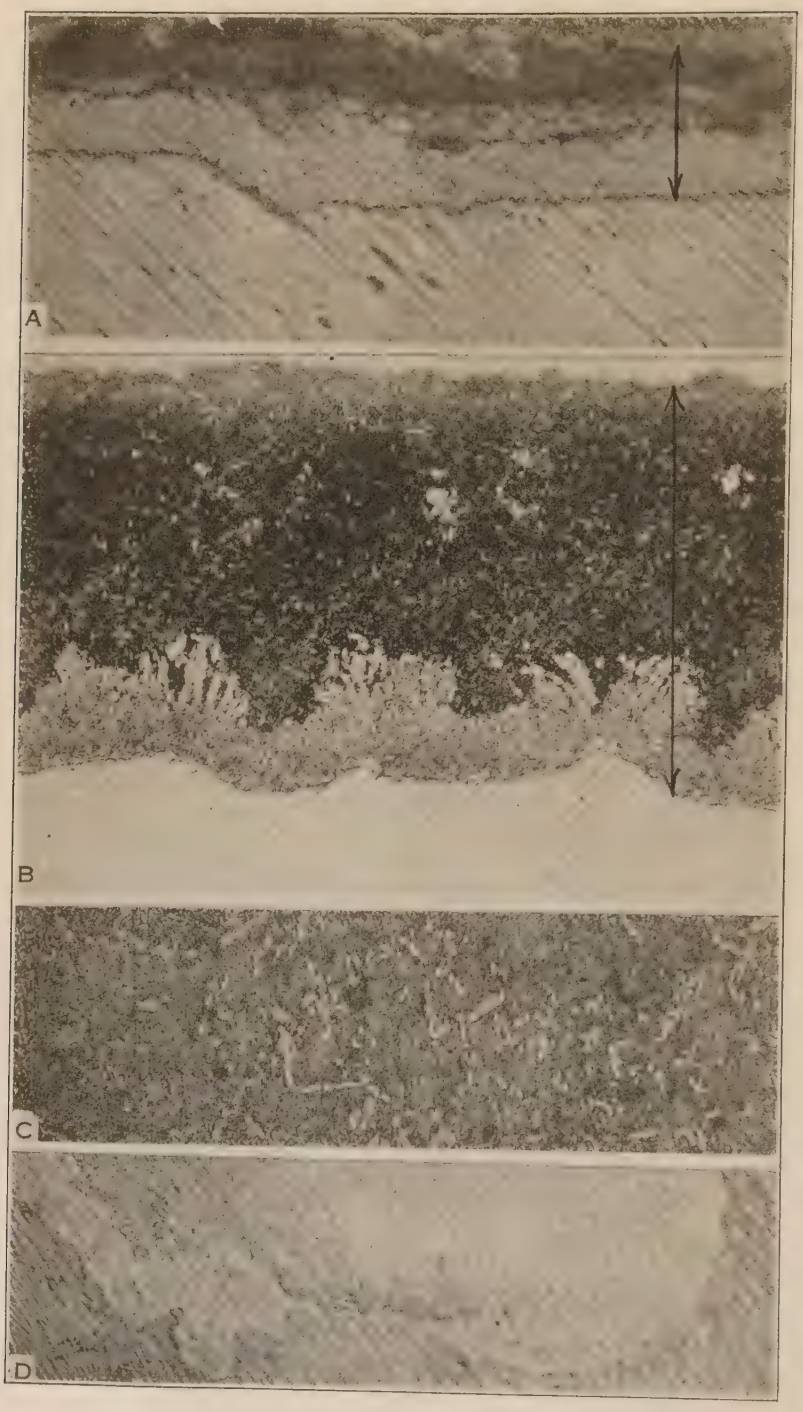

FIG. 26.

FIG. 26. Microstructure of two commercial hot-dipped zinc coatings, × 500. [B 113.] The arrows indicate the total thickness of the coating. Etchant, 1 per cent alcoholic solution of iodine.

A, Thin coating, average weight as determined by weighing the sheet before and after dipping, 1.37 ounces per square foot. The alloy layer (light colored portion) comprises the larger part of the coating.

B, Thick coating, average weight 2.5 ounces per square foot. Note the well developed fern-like pattern of the alloy layer, presumably this layer is $FeZn_7$.

C, Section through the zinc-rich outer portion of the coating of *B,* parallel to the surface. Note the crystals of the iron-bearing constituent embedded in the zinc-rich matrix.

D, An oblique section through the inner part of *B* at an angle of 5° (approximately) with the surface of the sheet, showing the innermost alloy layer, presumably $FeZn_3$.

content, the structure again becomes duplex by the appearance of crystals of a second compound, $FeZn_3$, having an iron content of approximately 22.2 per cent iron, this compound constituting the entire alloy. For the consideration of zinc coatings, we do not need to go beyond this point. In any fairly heavy zinc coating which has not been disturbed by wiping or in any other way during its setting, structural fields corresponding more or less definitely to the decrease in iron content of the coating from the surface of the base metal outward can be seen in a properly prepared cross section of the coating examined with the aid of the microscope.

The microstructural changes resulting from the gradual introduction of iron into zinc are shown in the micrographs of Figure 25 [B 113, M 19]. An iron wire was inserted in the center of a block of commercially pure zinc of a cross section 1 centimeter square (about 0.4 inch) and heated for four hours at 450° C., approximately 30 degrees above the melting point of zinc. The resulting structure (Fig. 25) shows that iron from the wire thoroughly permeated the surrounding zinc. There is no evidence that zinc had penetrated into the iron core, however, the line of demarcation between the iron wire and the alloys formed being definite and very clear. Immediately adjacent to the iron can be seen (Fig. 25*a*) a layer, presumably the compound $FeZn_3$, which has etching characteristics distinctly different from those of the next layer outward in which the definite form of the crystals is quite evident and which probably contains both of the compounds. Next in order away from the iron is a relatively thick layer constituting by far the greater part of the surrounding zinc and consisting of a soft matrix embedded in which are numerous small hard nodules corresponding to the constitutent *n*. Even in the outermost part of the zinc block, iron penetrated sufficiently to saturate the zinc as is shown by the presence of an occasional crystal of the zinc-iron compound.

The microstructure of coatings on steel sheets produced by zinc dipping under commercial conditions is shown in Figure 26. Figure 26*a* shows a coating of 1.37 ounces per square foot as determined by weighing the sheet before and after coating; Figure 26*b*, that of a much heavier coating, 2.5 ounces per square foot. (The values given for the weight of coating, in accordance with current commercial practice, include the coating on *both* sides of the sheet.) The variation in thickness of the coating was obtained by changing the setting of the exit rolls of the coating machine as previously indicated, other conditions in the bath remaining unchanged. It will be noted that in the thinner coating, the relative thickness of the alloy layer with respect to the entire coating

is very much greater than in the heavier coating. The crystalline form of the alloy layer in the thicker coating was not disturbed to the extent that it was in the thinner one; the total thickness of the alloy layer, however, does not appear very much greater.

Figure 16 shows the structure of two hot-dipped coatings produced on a commercial scale on sheet steel, but under unusual conditions. In producing the coating shown in *a*, the machine was stopped and the sheet kept stationary in the molten zinc bath for 2 minutes. The alloy, especially that immediately adjacent to the steel, presumably the $FeZn_3$ layer, developed exceptionally well under these conditions. The coating shown in *b* was produced by passing the same sheet four times through the zinc bath. As might be predicted the alloy layer under these conditions was also very well developed. The slight decrease in total thickness may have been caused by a slightly different setting of the exit rolls of the machine. The behavior of the sheets, produced under these unusual conditions, is of interest. After standing for a period of two weeks the surface was found to be covered with "flux spots" apparently caused by exudation of zinc chloride from the interior of the coating under the influence of atmospheric moisture.

The alloy layers in a zinc coating can be made more conspicuous by suitably annealing the coated material, which permits more iron from the base to diffuse into the zinc. Figure 27 shows the structural changes in the zinc coating on sheet iron which resulted upon annealing for different periods at 350° C. (670° F.).

The examination of zinc-dipped sheets which have been exposed to the weather for some time in an atmosphere relatively free from smoke often plainly shows the layers which go to make up these coatings. As the outer zinc-rich layer of the coating is slowly removed by atmospheric corrosive attack the dark-colored underlying alloy layer is revealed. The same result can be brought about by a carefully controlled attack with weak acid, and certain accelerated tests (Chapter 13) for zinc-coated products have been developed in accordance with this behavior.

The examination of galvanized sheets which have been slightly weathered often reveals many features which to one experienced in the manufacture of such material tell much concerning the preparation of the sheets. Lightly coated sheets after weathering often show transverse dark bands or "chatter marks". The dark bands are generally considered to be somewhat of the nature of ripples in the alloy layer, the formation of which was caused by the "chattering" of the machine. There is no evidence to indicate, however, that chatter marks are to be considered as serious defects.

Very heavy zinc coatings do not completely solidify for several seconds after the sheet leaves the bath. It sometimes happens that the coating flows slightly on the sheet and causes a roughened, rippled surface. Such coatings are often referred to as "slipped coatings".

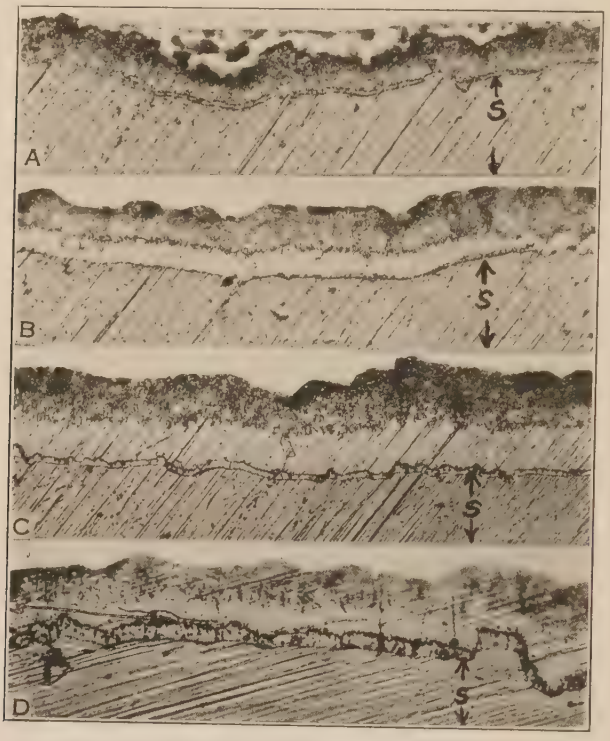

FIG. 27. Effect of annealing upon the alloy layers of a zinc coating, × 350. [B 121.] Etched as in Fig. 12.

A, commercial hot-dipped zinc coating on an iron sheet which is indicated by *S*; weight of coating, 1.25 oz. per sq. ft.

B, same as A after heating 2 hours at 350°C. Note how prominent the alloy layer is.

C, same as *A*, after heating 4 hours at 350°C. Note how the thickness of the second alloy layer has increased.

D, same as A after heating 5 hours at 350°C. The coating consists essentially of two alloy layers; the outer one corresponds rather closely to $FeZn_7$ in composition; the inner one, to $FeZn_3$.

The contact of the links of the chain used for conveying the sheet away from the pot as it emerges from the bath usually causes early freezing of the zinc coating at these contact points. Large, well-developed rosette crystals or spangles form around these spots and thus record the position of the conveyer chain on the sheet.

EFFECTS OF THE STRUCTURE ON THE BEHAVIOR OF COATINGS.

Since the advantage of zinc as a protective coating over most other metals depends primarily upon its anodic nature with respect to iron when both are exposed simultaneously in an electrolyte, any change in the composition or structure of zinc coatings which may affect this characteristic property of zinc is of importance. Vigouroux, Ducelliez, and Bourbon [B 108] have done most in providing the answer to the question as to the possible effect of the alloying of zinc with iron upon

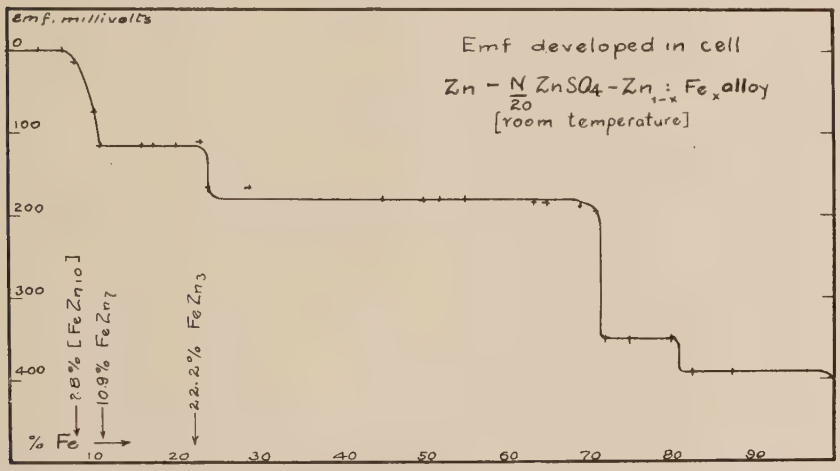

FIG. 28. Potential measurements of a series of cells of the type $Zn — \frac{N}{20} ZnSO_4 — Zn_{1-x} Fe_x$ alloy [B 108, B 105].

The e.m.f. between an electrode of zinc and an iron-zinc alloy, the composition of which was varied from 0 to 100 per cent iron, when both electrodes were immersed in $\frac{N}{20}$ $ZnSO_4$ solution, was measured.

the electrolytic solution potential of zinc. Their results in graphical form, as adapted by Guertler [B 105], are given in Figure 28, which is a summary of systematic potential measurements of cells of the type Zn–0.05*N* $ZnSO_4$–Zn:Fe alloys. The diagram has not been modified as yet to fit exactly the Zn–Fe equilibrium diagram (Fig. 11) but as it stands is of value in showing definitely that all of the alloys of the zinc-iron system behave in the same general manner toward iron that zinc does, that is, they are anodic, at least in ordinary aqueous solutions, though not to the same extent as zinc. The measurements of the electromotive force of the various alloys toward iron, both elements being immersed in 0.05*N* zinc sulfate solution and in external metallic con-

tact with each other, are intermediate between that of zinc and iron (0.4 volt approx.) and that of iron and iron (0.0 volt). In explanation of a diagram of this kind, it may be stated that in those cases in which an alloy is a duplex one, the potential measured is always that of the more reactive of the two constituents, in this case, the more anodic toward iron. Hence, in those portions of the diagram corresponding to the duplex alloys, the plotted line is theoretically always horizontal. An abrupt change in potential marks the disappearance of the more anodic constituent as the composition and structure change.

The evidence indicating the existing of definite compounds in the series of iron-zinc alloys, as shown by the electromotive force measurements, is stronger for $FeZn_3$ than for $FeZn_7$. In the former case, a very abrupt change occurs in the electromotive force-composition curve, while in the latter the change is much less abrupt, beginning approximately at the composition $FeZn_{10}$ and ending with that of $FeZn_7$.

The diagram shows that the compounds occurring in zinc-dipped coatings, $FeZn_7$ and $FeZn_3$, can be expected to exert a protective action on iron. On the other hand, both of these compounds are cathodic toward zinc, and hence when exposed to corrosive conditions simultaneously with the outer zinc-rich layer will tend to hasten any corrosive attack of the latter. This action is slight, however, and can for most purposes be disregarded.

The effect of the structural modifications resulting from the introduction of iron into the zinc upon the mechanical properties of the coating are much more pronounced, however. A considerable degree of ductility is necessary in the coating when the coated material, such as sheet or wire, must withstand severe deformation in the process of fabrication of the finished articles made from such materials. Both of the zinc-iron compounds, $FeZn_7$ and $FeZn_3$, are relatively hard and brittle as compared with zinc, and the coating of which they form a part will necessarily show these same properties to a considerable extent. Coatings in which the alloy layers are well developed will, as a rule, flake readily from the iron base when the latter is severely bent.

Finkeldey [B 94, B 121] has reported that the surface character of the alloy layer has a pronounced influence upon the brittleness of a hot-dipped zinc coating as a whole, as exhibited upon bending. Coatings in which the crystalline form of the alloy layer is well developed and the contour of the surface of the alloy layer is irregular because of the fern-like growths (Fig. 16*b*) prove, under test, to be much more brittle than coatings of similar weight, in which the contour of the alloy layer is smoother and more regular. Farnesworth [B 94] has also made observations which confirm this. Other evidence has been re-

ported (p. 98) which indicates that the physical character of the alloy layer determines the behavior of the coating on bending as much as, if not more than, the total amount of the alloy layer present. Whenever practicable, it is advisable to carry out the zinc-coating operation after all forming operations of fabrication have been completed.

The peeling of galvanized or zinc-dipped coatings when heated repeatedly, usually under oxidizing conditions at a slightly elevated temperature but still very considerably below the melting point of zinc, has been known for a good many years [B 3]. The "smoke pipe" in the ordinary household furnace often affords a good example of this. Arthur and Walker [B 106] concluded that this behavior of zinc coatings is not caused entirely by oxidation. They reported that it occurred when they heated specimens in hydrogen and in carbon monoxide to approximately 350° C. The peeling of the coating is related to the growth of the alloy layer which occurs when the coating is heated, as discussed below. When the coating peels, the surface of the alloy layer is revealed rather than that of the base metal.

Modifications of the Hot-dipping Process.

The essentials of this process have not been changed materially since its inception. The high degree to which the mechanical features of the process have been developed have not necessitated any vital changes in the procedure. Various minor modifications have been made from time to time, the aluminum treatment of the zinc bath being a noteworthy case. A modification recently advocated by Bablik and stated to be used very considerably in Austria [B 80] has for its object the minimizing of the alloy formation in zinc-dipped coatings. He has described the use of a lead bath with a relatively thin layer of zinc on the top. The material to be coated is inserted through the flux directly into the lead and is then brought out through the layer of molten zinc. This method is essentially the same as that which has been used for many years in America for producing a special lightly coated sheet used for forming operations. For this purpose, according to Camp and Francis [B 95], the amount of lead in the ordinary "pot" is increased up to the level of the bottom of the flux box, thus leaving a layer of zinc of only a few inches. The coatings from such a bath contain very little of the alloy layer and are sometimes spoken of as "lead and zinc" coatings. The process is a rather difficult one to carry out efficiently, however.

Other methods [B 51] proposed for reducing the contamination of the zinc by iron are based upon the use of a refractory lining of the

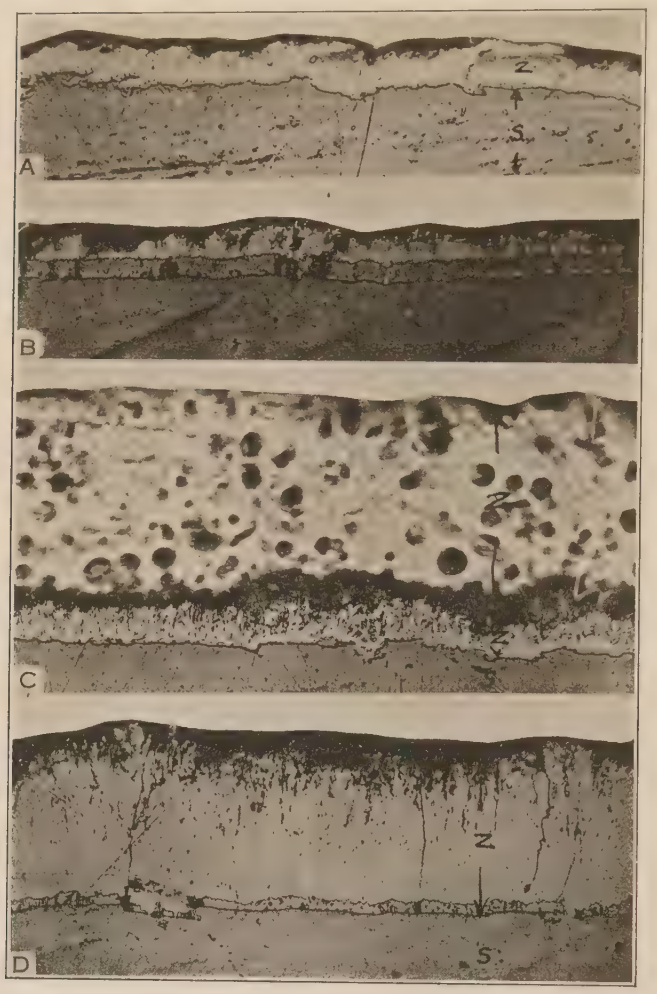

FIG. 29. Effect of heat treatment upon the structure of the coating of commercial galvanized sheet steel; × 500, Etched as in Fig. 12.

A, light coating; 0.87 oz. per sq. ft. Note that the coating as made consisted largely of the alloy layer, *S* indicates the steel base.

B, same as *A* after 30 minutes at 500°C. Note how prominent the second or inner alloy layer ($FeZn_3$), has been rendered.

C, heavy coating, 2.54°C. per sq. ft. The zinc-rich layer, *z*, comprises greater part of the coating.

D, same as *C* after 30 minutes at 500°C. The outer alloy layer has increased decidedly in thickness at the expense of the zinc-rich layer, and the inner alloy layer has also become prominent.

steel container where it is in contact with the zinc, all of the heat to be transmitted to the zinc from the lead layer below.

Various heat-treatment processes intended for the improvement of hot-dipped zinc coatings have been patented. By simply annealing such coatings a pronounced change in the microstructure and properties can be brought about. If the annealing is done at a relatively low temperature, it is necessary to protect the zinc coating against oxidation and peeling during the long heating period required. This can be done by packing the samples in zinc dust or powdered charcoal. The same result can be attained in a shorter time at a higher temperature, although the conditions which are best for heat treatment of any given sample are dependent somewhat upon the character of the base metal [M 24]. Figure 29 shows how the thickness of the alloy layers in the coating on two galvanized sheets differing in their initial weight of coating was decidedly augmented when heated for 30 minutes at 500° C., a temperature considerably higher than the melting point of zinc (419.4° C.). Such material, as a rule, will flake upon bending on account of the thick irregular alloy layers and most of the proposed "improvements" of galvanized coatings by heat treatment of this kind have found no commercial application.

A recent process to which the rather fantastic name of "galvannealing" has been applied by its promoters seems to be a possible exception, however. In this process, the commercial application of which so far has been confined largely to wire [B 91] although it has been applied successfully to sheets, the "unwiped" wire immediately after leaving the zinc bath is passed through a tubular furnace at approximately 675° C. (1250° F.). This temperature may be varied somewhat according to the size of the wire. The resulting coating, which is claimed to be as heavy as that on the ordinary unwiped wire and to have as good bending properties as that on a "tight wiped" wire, has a very smooth surface, and is very uniformly distributed around the wire. The iron content of the coating is raised considerably by this treatment. The usual product averages between 7 and 8.5 per cent of iron. Figure 30 shows the structure of a heat-treated zinc coating of this kind on wire. According to what has been said previously concerning the relative electrolytic solution potential of the zinc-iron alloys as compared to that of zinc, it would be expected that the corrosion resistance of this type of coating would be good. Extensive atmospheric exposure tests are necessary, however, before a final answer can be given on this point. The mechanical properties, on the other hand, particularly the resistance to flaking on bending, would hardly be expected to be improved, although the claim has been made [B 91] that the properties are not adversely

affected. Figure 30*b* shows how, when such a coated wire is bent, a series of very fine cracks is produced instead of a pronounced flaking. In addition to the augmented alloying effect of the iron and zinc of the coating which would result from the heat treatment applied, it might be expected that the rather pronounced stratification usually found in the ordinary coatings would be eliminated to a large extent. A structural change of this kind would offset, to a large extent, the undesirable effect of the increased alloying, provided the coatings are not too high in iron.

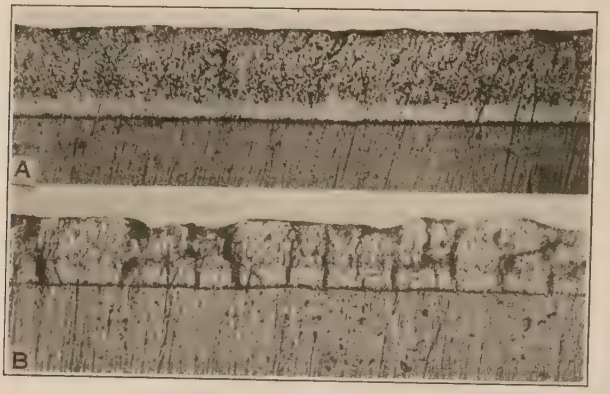

FIG. 30. Structure of an 'unwiped' hot-dipped zinc coating, heat-treated subsequently to the dipping operation ("galvannealed" wire), × 350, etched as in Fig. 12 [B 121].

A, The iron zinc alloy layer comprises the entire coating; weight of coating 0.6 oz. per sq. ft. of surface.

B, same as A after bending around a wire of the same diameter. Note the numerous fine cracks but no pronounced flaking occurred, however.

Likewise, the smooth even surface of the alloy layer in such a coating would be expected to reduce its tendency to flake when the material is bent. The matter is still somewhat of an open question, however.

Very superior bending properties have also been claimed for wire coated by a new process, in which the wire is given a slight carburizing treatment prior to being zinc-coated [B 96]. This superiority may perhaps be attributable to the character of the surface resulting from the action of the zinc on the carburized layer. It has already been mentioned that molten zinc attacks high-carbon steel very differently from low-carbon steel. Figure 63 illustrates differences in flaking of the zinc coating of galvanized wires of different compositions.

BY-PRODUCTS.

The by-products of the hot-dipping process will be mentioned only briefly. Breuil [B 74] states that, as a rule, of the zinc in the molten

bath, 68 per cent is deposited as coating on the articles immersed, 2 per cent is lost by volatilization, 18 per cent alloys with iron and forms dross and 12 per cent is oxidized. In the modern plant, especially if run on a large scale, the efficiency is much better than this, although Camp and Francis [B 95] state that even here the loss of zinc as dross is frequently as high as 10 per cent. The oxide which is skimmed off from the surface of the bath is sold as "zinc ashes" and the metal is recovered by reduction of the oxide. The dross is bailed out from the bottom of the bath with a perforated dipper at stated intervals. It has an average iron content of 2 to 5 per cent. Some of the zinc-iron alloy is used as such in the preparation of other alloys in which both zinc and iron are desired. Much of the zinc, in a fairly pure state, may be recovered from the dross by a liquation process known as "sweating". Upon heating the alloy, two distinct layers are formed, the lower one being of the higher iron content, 7.5 to 9 per cent according to Smith [B 18]. The upper or zinc-rich layer is skimmed off. In order to recover all the zinc from the iron-zinc alloy, a special process of redistillation is necessary.

In addition to the zinc products, the spent flux or sal ammoniac skimmings have a salable value. These skimmings consist principally of zinc oxide, zinc chloride and some ammonium chloride together with miscellaneous dirt accumulated during the process.

Mechanical Treatment of Coatings.

The mechanical treatment of commercial zinc, particularly that on sheets coated by the dipping process, has often been considered as a means for improving the properties of such coatings, especially for rendering them more ductile. Such attempts to improve the properties of hot-dipped coatings by any simple process of mechanical working have not proved successful so far. Burgess [B 3] showed years ago, that by passing sheets, zinc-coated by hot-dipping, through rolls set so as to reduce the thickness by approximately 0.01 inch, the coating could easily be stripped from the base in relatively large flakes. Electroplated coatings, on the other hand, could be separated from their base after being cold-rolled in this manner only by repeated bending of the sheet. It may be concluded, therefore, that the zinc-dipped coatings in general are not susceptible to any appreciable amount of mechanical after-treatment. Especially is this true for coatings in which the alloy layer is fairly well developed.

If the deformation is done at a temperature considerably above ordinary room temperature, the flaking of the coating is reduced very considerably. For this reason, it is usually recommended that galvanized pipe be bent at a temperature of 95° to 150° C. (200°-300° F.)

[A 25, p. 312]. The pipe may readily be maintained at a suitable temperature by passing steam through it. Electroplated zinc-coated articles will withstand very considerable deformation. To a very limited extent, for some stamping operations in which it is considered desirable to have the coating done prior to the forming operations, steel sheets which have been zinc-coated by electroplating are used. Zinc-plated wires are also sometimes drawn down slightly subsequently to the electroplating operation.

Effect of the Hot-dipping Process on the Base Metal.

The reported detrimental effects on the base metal caused by hot-dipping are more properly to be attributed to some of the incidentals of the process rather than to the effect of the molten zinc itself. It is a well established fact that brittleness can be induced in steel as a result of pickling in acid although the change, in general, is of a temporary nature [O 1, O 2, O 3, O 17]. It has also been claimed [B 129] that inferior tensile and torsional properties found in some wire coated with zinc by means of hot dipping were to be attributed to hydrogen retained by the metal. No well substantiated case of this kind has ever been reported, however. The greater part of the hydrogen in the steel to which the brittleness is usually attributed is driven off at a rather low temperature, approximately 200° C., so that it is extremely improbable that at the temperatures employed in the hot-dipping process, an amount great enough to affect the mechanical properties of the metal would remain in the steel. The following results by Lange [B 24] on samples of wire of the same reel are representative of the changes in the mechanical properties of the base metal which may be expected as a result of zinc dipping.

Brittleness of malleable iron castings coated by zinc-dipping often causes a good deal of concern to manufacturers of such materials. It has been definitely shown, however, by Marshall [B 140] and by Bean [B 139] that the heat-treatment effect incidental to the hot-dipping process, especially the quenching of the articles after they have been dipped, is responsible for the brittleness rather than any effect of the zinc *per se*. Certain features of the chemical composition of the malleable iron also appear to play an important part in rendering some irons more prone to brittleness than others. Brittleness of cold-worked sheet steel after galvanizing, such as articles stamped out of sheet steel, has also been reported. This also is probably to be attributed to the heating of the hot-dipping process rather than to any specific effect of the zinc itself.

The annealing action of the molten metal bath, of course, cannot be

TABLE 5.—STRENGTH OF WIRE BEFORE AND AFTER ZINC-COATING [B 24].

Electro plated [1]			Hot-dipped			No coating applied		
Spec. No.	Tensile Strength [2]	Elongation	Spec. No.	Tensile Strength [2]	Elongation	Spec.	Tensile Strength [2]	Elongation
	Kg./mm.²	Per cent		Kg./mm.²	Per cent		Kg./mm.²	Per cent
1	252	1.0	1	166	5.2	As received	199	2.6
2	249	0.9	2	168	5.8			
3	228	1.4	3	193	4.5	Tempered 300° C.	200	5.4
4	182	2.1	4	168	7.1			
5	201	1.3	5	140	6.4	Tempered 450° C.	131	3.6
6	207	1.6						
7	193	1.8						
8	198	3.0						
9	178	3.7						

[1] The electroplated wire was evidently tested soon after being plated.
[2] Conversion factor—lbs. per sq. in., multiply by 1422.5.

avoided. Hence, the hot-dipping process is not suitable for coating articles of which the properties would be seriously impaired by the hot metal, such as springs. The amount of such work is very limited and such parts are usually small; electroplating is a more convenient method to use in every way.

PAINTING OF ZINC-COATED SHEETS.

Painting of zinc-coated sheet products, such as are used in building construction, is often desirable and necessary. It is well known, however, that the paint does not hold satisfactorily to such surfaces unless they have been well weathered, but soon chips and peels. In order to furnish the mechanical bond necessary for holding the paint, such zinc-dipped sheets must have the surface roughened somewhat, either by allowing them to weather and become roughened by atmospheric corrosion or by roughening artificially by swabbing on a solution which will dissolve some of the zinc. A dilute solution of copper acetate is commonly used for this purpose, although the sulfate, chloride, or nitrate are also suitable. Any solution having a solvent action on the zinc, such as dilute hydrochloric acid, can be used [B 146].

The degree of adherence of paint to galvanized iron seems also to depend somewhat upon the nature of the paint used as a primer coat. Paints whose pigment consists largely of zinc dust and zinc oxide have been reported to show a marked superiority over other metal primers in

their adherence to galvanized iron. If galvanized materials are to be used in a very corrosive atmosphere, that is, one contaminated with acid gases such as sulfur dioxide, the zinc coating should by all means be kept well painted.

Surface Appearance of Zinc-coated Sheets after Storage.

The surface appearance of galvanized sheets after being stacked together either in transit or in storage for a considerable time, especially in very humid atmospheres and near the sea, is often spoiled by the formation of a white bloom which is distinctly different from flux spots or similar defects arising in the dipping process. Such materials are not infrequently rejected upon receipt of the shipment although there is nothing in the literature on this subject which would indicate that in general the change is anything more than a slight surface corrosion of the zinc coating. The presence of lead in the zinc coating is considered by some to contribute to this behavior of the coating. Evans [A 20, p. 79] has shown that the explanation he has given of the function of oxygen in the phenomenon of corrosion in general is applicable to this case. In the inaccessible parts of the stack where the sheets are in intimate contact with one another, the oxygen concentration is less than in the more open parts. Hence, such portions of the metal surface are anodic with respect to those portions which have free access to the air. The zinc is corroded, therefore, as moisture condenses on the surface of the sheets to form zinc hydroxide which constitutes the white bloom. Pronounced corrosion resulting in serious defects of the zinc coating from this cause is not common, however, unless the exposure conditions are very severe such as those reported by Arguelles [B 134] for stacks of galvanized sheets left exposed to the weather in the Philippines, in which case very severe corrosion resulted in the inner portions of the pack.

Toxic Properties of Zinc.

Much has been written, pro and con, concerning the toxic properties of zinc, especially when in soluble form. Conclusions diametrically opposed to each other have been expressed. Evidence has been brought forward in support of the claim that zinc is one of the elements normally found in the human body and most other animal and plant tissues. The conclusion seems to be warranted that a small amount of zinc may be necessary for the proper functioning of the animal system, but that beyond a certain limit a toxic effect is to be expected. An amount of zinc up to 23 parts per million in drinking water [B 123, B 124] has been stated to be harmless. In the past there has been considerable dis-

cussion as to the advisability of using zinc-coated pipes in water systems. They are in very common use now, however, without any ill affect being attributed to them.

Distilled water and rain water have a greater corrosive effect than does the ordinary tap water. Water containing carbon dioxide, as might be expected, attacks zinc much more than water free from this gas. Likewise, water that has been treated with chlorine attacks zinc more rapidly than untreated water. Lothian and Ward [B 138] have stated that raw (untreated) water dissolved only 4 parts per million of zinc from a new zinc-lined tank in 24 hours, whereas chlorinated water dissolved 20 parts per million in the same time. If a fresh supply of chlorinated water constantly passes through such a tank the attack of the zinc is maintained. However, if the water is merely stored, the attack diminishes as a protective surface film, presumably of zinc hydroxide, is formed.

It is generally recognized, however, that zinc-coated dishes are not at all suitable for use in the preparation of foods. This is particularly true for materials containing acids. The use of zinc-coated containers, pails, tubs, and the like, in making lemonade and similar drinks, as used to be not infrequently the case for large public gatherings, especially is to be guarded against. The investigation of Bernard and Bishop [B 125] for the Indiana State Board of Health on this subject resulted in legislation in that state making it unlawful to use such zinc-coated containers for acid drinks. Similar legislation in Holland prohibiting the use of zinc-coated dishes for the preparation of foods in general has been reported.

Recent tests by the Bureau of Chemistry of root beer which was suspected as being the cause of numerous cases of slight poisoning indicated that the beverage contained 229 milligrams of zinc per liter. Supplementary tests by Sale and Badger [B 142] to show the rate at which various liquids would dissolve zinc when allowed to stand in a zinc-coated pail gave the results summarized in Table 6.

TABLE 6.—ZINC DISSOLVED FROM ZINC-COATED IRON PAILS, HOT-DIPPED COATING [B 142].

Liquid	Zinc, mg./liter After 17 Hours	Zinc, mg./liter After 41 Hours
Tap water (Washington, D. C.)	5	21
Distilled water	9	27
Carbonated water	193	181
Milk	483	1054
Orangeade	540	854
Lemonade	1411	2700

Chapter 7.

Zinc-coating by Cementation, Electroplating and Other Methods. Comparison of Coatings Made by Various Methods.

Zinc Cementation.

Historical: The production of one important class of zinc coatings on iron and steel depends upon the utilization of the principle of cementation. The process is generally known commercially as "sheradizing", the name being formed from that of the originator of the method, Sherard Cowper-Coles. The process dates from 1900 [B 177] when coatings of this kind were produced unintentioally during the annealing of some iron and steel samples while packed in zinc dust, the zinc being used as a supposedly inert substance for packing, in order to exclude the air.

It has already been pointed out, however, that the alloying of metals by means of cementation was known many years before it was utilized for the production of zinc coatings. Sang, in his review of metallic cementation [B 157] states that the first patent for the production of metallic coatings by this means was that of Miles Berry, an Englishman, in 1838, who proposed to produce copper coatings on iron by cementation for the purpose of protection from corrosion. Various other attempts were made subsequent to this but the development of the sherardizing method is the first important and commercially successful application of the principle of cementation to the production of metallic coatings.

Outline of the Process.

As will be seen from the description below, this process is particularly well suited for small articles such as bolts, screws, nuts, small castings and the like. It is used commercially to a considerable extent for electrical conduits, to an extremely limited extent for sheets and not at all for wire although considerable has been written on the possibility of applying the process, in slightly modified form, to the zinc coating of wire [B 159, B 163].

The articles to be coated, after cleaning, which as a rule need not be so drastic as for some other coating methods [B 157], are packed in zinc dust in a metal drum which may serve also as the shell of the furnace if the heating is to be carried out electrically. The container must be reasonably air-tight and be fitted with a tightly fitting cover. The container together with its contents is heated either electrically by heating coils in its walls or by gas, and is slowly rotated during the heating. Care is taken that the zinc-dust packing does not completely fill the container, so that as the drum is rotated a slight "rumbling" between the zinc dust and the articles to be coated occurs and intimate contact between the two results. This feature of operation is important as the uniformity of the coating produced depends to a very large extent upon it. The character of the zinc dust used, particularly its iron content, and the temperature and period of heating, also have an important effect upon the coating produced. Fine zinc powder absorbs moisture rather readily, and on heating, hydrogen is evolved according to Johnson and Woolrich [B 166]. The evolution of hydrogen by the heated powder is an advantage rather than otherwise as it reduces the chances for oxidation.

Commercial "blue dust", a by-product in the usual method for smelting zinc, is the material used generally, although a special form of zinc powdered to 100-mesh fineness is used to some extent in combination with the blue dust. The blue dust contains, according to Sang [B 157], approximately 85 to 90 per cent metallic zinc, with 5 to 8 per cent of zinc oxide. A zinc-iron alloy of the approximate composition, $FeZn_{10}$ [B 173], somewhat of the nature of the dross formed in the hot-dipping process, is also used to a limited extent. In some of the earlier descriptions of the process the dilution of the zinc dust by some inert material, such as sand, has been emphasized [B 154, B 162]. The principal reason for an addition of this kind is to prevent caking of the extremely fine dust. The practice of some of the most successful users of this process has not favored the dilution of the zinc dust but rather the addition at intervals of a small amount of new dust to the used dust. The use of 10 per cent new dust and 90 per cent of used material, carefully freed from iron and oxide particles, has been found to give excellent results [B 171]. According to Storey [B 173], such a mixture of used and new dust would have a metallic zinc content of 80 to 92 per cent.

Effect of Temperature.

The temperature at which the cementation process is carried out has a marked effect upon the rate of coating-formation. This is shown in

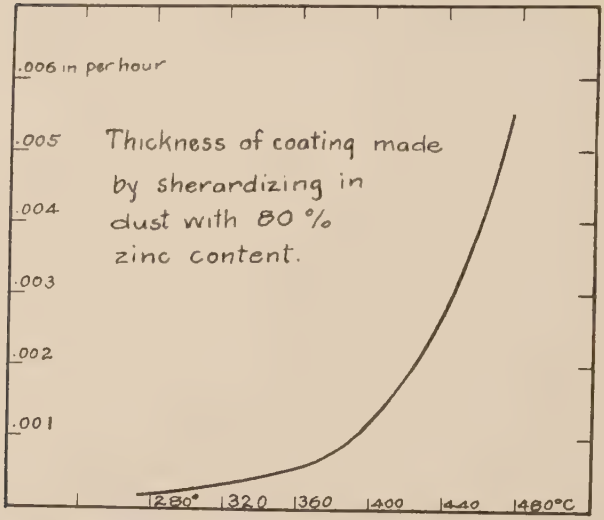

FIG. 31. Effect of temperature upon the thickness of the coating produced on iron by zinc cementation [B 171].

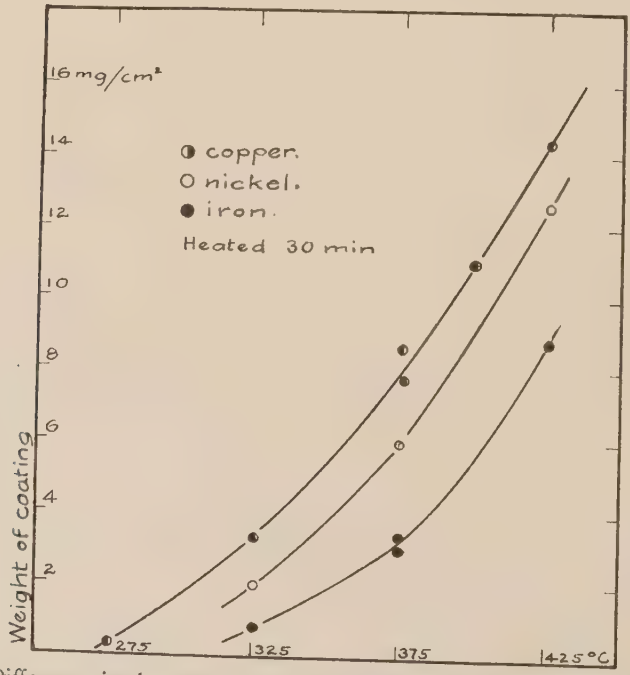

FIG. 32. Difference in the rate of coating-formation for different metals heated in zinc dust [B 166].

10 mg/cm² in 30 minutes is equivalent to 0.0011 inch per hour (approximately).

Figures 31 and 32. A characteristic property of the fine zinc dust used is that it does not melt readily when heated somewhat above the melting point of zinc. Each microscopic particle of zinc undoubtedly does melt, but the particles do not coalesce to form a melt of any appreciable size. This is usually attributed to the influence of a pellicle of oxide surrounding each dust particle. It is possible, therefore, for the cementa-

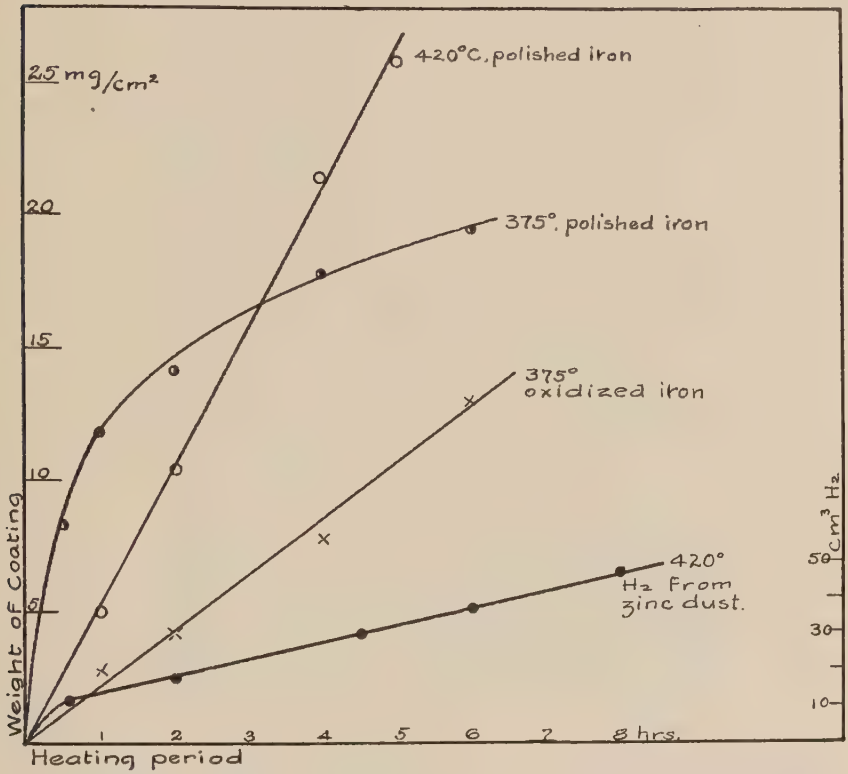

FIG. 33. Effect of the cementation period upon the rate of coating-formation [B 166].

tion process to be carried on at a temperature considerably above 419° C., the melting point of zinc. The appearance and properties of the coating vary with the temperature used. For most purposes a rather low temperature is favored, and 350° to 375° C. has been recommended as very desirable [B 171]. Sang [B 157] characterizes zinc cementation above the melting point of zinc as a special modification of the hot-dipping process and it is probably true that when the temperature exceeds 419° C., in addition to the process which takes place below

419°, particles of zinc become attached bodily to the surface of the article and aid in that way in building up the coating.

The temperature used also affects the iron content of the coating. A sherardized coating produced at relatively high temperatures has a considerably higher iron content than does one made at a lower temperature, other conditions of operation remaining the same. The temperature to be used also depends somewhat upon the composition of the zinc dust used. McCulloch [B 174] found that, with a dust having an iron content of 7 per cent, it was necessary to maintain the temperature at 450° C. (842° F.) in order to deposit a coating at the same rate as was produced from a pure zinc dust at 375° C. (707° F.). This also applies in the case of the zinc-dross powder sometimes used for sherardizing. Presumably this difference in the sherardizing temperature is a result of the somewhat lower vapor pressure of the zinc-iron alloy as compared with that of pure zinc.

The effect of the duration of the process upon the coating produced is shown in Figure 33 from the work of Johnson and Woolrich [B 166].

Structure of Coating.

The coating produced on iron by zinc cementation consists of fairly well-defined layers, if we disregard the rough outer portion of the coating which, to a large extent, appears to be built up mechanically. In coatings made at rather low temperature, for example 350° C. or below, the greater part of the coating is a single-phase layer which appears to correspond to the field *n* of the iron-zinc equilibrium diagram (Fig. 11). McCulloch states [B 174] that the minimum iron content of a sherardized coating is approximately 6 per cent. According to his experiments, the alloy formed by heating iron foil in zinc dust for 45 days at 415° C. contained 6.15 per cent iron and an almost identical result was obtained by heating iron foil in zinc dust for 2 days at 365° C. This, however, does not controvert the usual assumption concerning the structure of such coatings. The result was interpreted by McCulloch as showing that the limit of the iron-zinc solid solution (constituent *n* of the diagram) corresponds to approximately 6 per cent of iron instead of the higher percentage usually given. The average iron content of a sherardized coating is always considerably higher than the minimum given by McCulloch. According to Burgess [B 161] and Storey [B 173] the main layer of the coating has a composition indicated quite closely by the formula, $FeZn_{10}$ (7.8% Fe). Further evidence is required to confirm this point, however. McCulloch gives 8 to 10 per cent as the average iron content of sherardized coatings. Sometimes a second layer can be detected between the main layer of the coating and the iron

base and, as the iron content of the coating is increased, generally as a result of a higher cementation temperature, this layer becomes more conspicuous. It is of a higher iron content and perhaps corresponds to

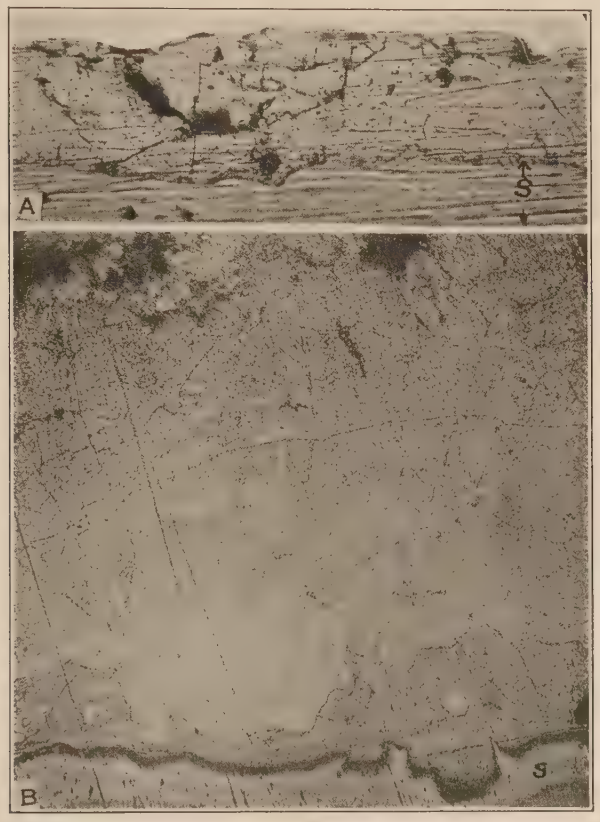

Fig. 34. Microstructure of sherardized zinc coatings.

A, Cross-section of a coating, 0.9 oz. per sq. ft., produced by sherardizing. *S* indicates the base metal. The fissured appearance is characteristic of coatings of this kind. The entire coating is made up of zinc-iron alloy. × 350. Etched as in Figure 12 [121].

B, Oblique section of a sherardized coating, × 100. Note the two layers [B 113].

the compound, $FeZn_3$, indicated in the equilibrium diagram of the zinc-iron alloy system.

It is to be expected that as either the temperature or the period of cementation is increased, the iron content of the principal, or outer, alloy layer will increase in accordance with the equilibrium diagram for the iron-zinc system of alloys. The formation of a well-defined second (iron-rich) layer adjacent to the iron base is hardly to be expected until

at least the inner portions of the first layer are fully saturated with iron. This would imply a composition corresponding to $FeZn_7$ in much of this layer.

Figure 34 shows the microstructure of a sherardized coating. It will be noted that almost the entire coating is made up of one layer which has a characteristic fissured appearance. The outer part of this layer is

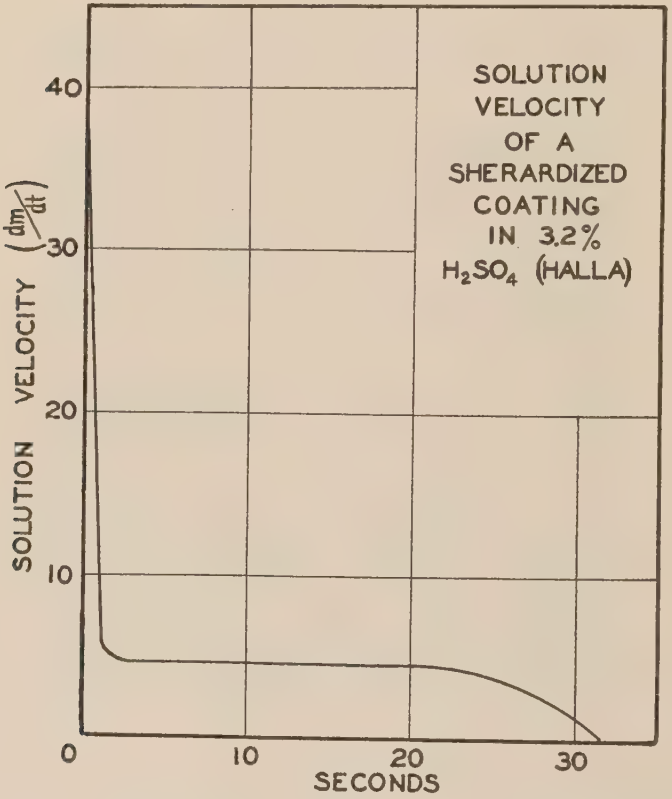

FIG. 35.—Rate of solution of a sherardized coating in dilute acid (B 168).

rough and contains mechanically entrained inclusions, and on the inner side a very much thinner second layer exists.

The results obtained by Halla [B 168] on the "solution velocity" of sherardized coatings in dilute sulfuric acid confirm the conclusion based on examination of the microstructure that the bulk of any such coating is made up of a single and apparently uniform layer. Nails sherardized under various conditions were used by Halla as material. Those used

for the results in Figure 35 were heated for 3 hours at 365° C. in the zinc dust. From the loss-of-weight curves of the specimens immersed for given periods in the acid, Halla determined the "solution velocity" by graphical differentiation. Figure 35 shows that as the porous outer layer, high in entrained particles of zinc dust, is dissolved the velocity of solution drops to a relatively low value and remains fairly constant for the rest of the coating, thus indicating uniformity of structure and composition for the coating as a whole.

Mechanism of the Zinc Cementation Process.

As has been previously stated, difference of opinion concerning the nature of the cementation process exists. All agree that once the zinc is deposited on the surface of the iron article embedded in the zinc dust, alloying results by diffusion in the solid state. The method by which the zinc is deposited on the surface is the disputed point. Some [B 157, B 174] consider that the slight vaporization of the zinc which occurs even at the relatively low temperature used in this process is sufficient to account for the transportation of the zinc from the dust particles to the iron surface. Others [B 162, B 173] hold that *intimate* contact of the zinc particles and the iron surface is sufficient, and that the zinc particles become attached bodily to the surface. The discussion is one of academic rather than practical interest. Both factors undoubtedly contribute to the coating process as carried out in practice.

Johnson and Woolrich [B 166] found that with relatively coarse zinc dust (100 to 150 mesh) they obtained more rapid deposition of the zinc coating than with extremely fine dust. At 370° C., without tumbling, a coating was built up by the coarser dust about twice as rapidly as with the fine material. The coating, however, was quite porous and lacked the uniform smooth surface characteristic of those made by the use of the very fine dust.

Attempts have been made [B 155, B 160] to develop a zinc-coating method based strictly upon the action of zinc vapor, the articles being placed in a drum of wire netting and rotated in an atmosphere of zinc vapor and some reducing gas such as hydrogen. A process of this kind described by Cowper-Coles was termed "cowperizing" and one by Sang, "vapor galvanizing". Neither one met with favor nor proved practicable in a commercial way as did the regular zinc cementation process.

Service Behavior of Cementation Coatings.

Since the coating produced by cementation is essentially a zinc-iron alloy, the results obtained in service with such coatings differ in many respects from those with the other types. As shown in Figure 28, the

zinc-iron alloys behave, in an electrochemical way, toward iron the same as zinc does. That is, all are anodic toward iron when in contact with it and immersed in an electrolyte, but to a smaller degree, than pure zinc is. It is to be expected, therefore, that zinc coatings produced by zinc cementation will afford electrochemical protection to iron and steel.

As weathering occurs and zinc is oxidized, the coating gradually assumes a dark appearance as the iron is likewise oxidized. The surface of the articles finally becomes very dark gray and almost black if the iron content of the coating is not too high. Coatings high in iron, and hence containing the iron-rich compound, usually show a red dusty surface upon weathering from the ferric oxide produced. A wrong impression is often formed concerning such coatings, that is, that the coating has been entirely corroded away and the red rust indicates an exposure of the base metal. It can generally be shown readily that such is not the case. Storey [B 173], however, states that such coatings are not nearly so resistant to atmospheric attack as those of a lower iron content which form the smooth black oxide finish as they weather.

McCulloch [B 174] found that "coatings formed in dust containing 11 per cent iron rusted immediately in salt spray while coatings formed in dust with 9 per cent iron showed good resistance". From other data given by him, it appears that the average iron content of coatings made under such conditions were 14.9 and 11.1 per cent, respectively. This agrees with the statement of Storey [B 173] that with an iron content of 15 per cent the resistance of the coating to atmospheric corrosion is very low. This difference in service life is to be attributed largely to the difference in the nature of the iron oxide coating formed in two cases rather than to the relative electrochemical nature of the two. In the case of the coatings low in iron, a closely adhering protective layer of iron oxide is formed, whereas the corrosion of the high-iron layer results in loosely adhering flocculent rust which affords little if any protection to the metal beneath.

If the zinc dust used is high in iron, particles of iron are often mechanically enclosed in the outer layer of the coating. Rusting occurs readily when the coating is weathered and gives the same red rusty appearance.

On the whole, the coating produced by cementation may be considered as corresponding rather closely in composition and properties to the alloy layer of the zinc-dipped coating.

For general all-round service, a coating 0.0025 inch in thickness has been recommended as ample after a good deal of experimentation and testing [B 171, B 178]. Such a coating represents approximately 3 hours' heating at 375° C. in a dust of high metallic zinc content (Fig.

31). Such coatings should withstand 170 hours' exposure in the salt spray test using a 2½ per cent sodium chloride solution before rusting of the underlying metal begins.

Electroplated Zinc Coatings.

The application of electrodeposition for the production of zinc coatings is of a very considerable commercial importance. On account of its exceptionally high overvoltage, zinc can readily be deposited electrolytically from aqueous solutions usually with high current efficiency, although its position in the electrochemical series would suggest otherwise. As a rule, the process is used for coating finished articles rather than for semi-finished materials such as sheet, wire, and pipe, although very considerable quantities of wire products are coated in this way. Zinc plating is used practically exclusively for coating iron-wire screen cloth. According to Camp and Francis [B 95] only very limited quantities of ordinary wire are coated by electroplating, but for flat wire and steel strip, hot-dipping followed by "wiping" is so much more expensive than electroplating that the latter process is used. It is also used somewhat for pipe, particularly for electrical conduits for interior use. The application of electroplating for sheets is very limited, however [B 197]. A special application of zinc plating suggested by Speller [A 25, p. 317], for coating pipe couplings for the particular purpose of preventing "galling" of the threads is now being extensively used.

Mechanical Equipment Required.

Mechanical devices and automatic equipment for zinc electroplating have been developed to a very high degree of efficiency so that very little attention is required for their operation. The equipment varies according to the materials to be coated, but most of it is of one or the other of two general types, which may be designated as the "barrel" type and the "conveyer" type.

For zinc plating small articles, such as bolts, nuts, screws, nails, washers, and in fact, all small articles which do not need to be handled individually in the plating bath the barrel method, or a modification of it, is used. A perforated barrel made of some nonconducting material is immersed in the solution of the zinc salts, the electrolyte, and enough of the articles, properly cleaned, to fill the barrel partially, are placed within. They are in contact with flexible metal conductors on the inside of the barrel and together they form the cathode of the cell. The anodes, of cast zinc, are hung in the solution just outside the barrel and sometimes partially encircle it. The barrel is supported in the solution usually with its longitudinal axis horizontal and in a manner such that

it can be rotated about this axis. As the plating process proceeds the barrel is slowly rotated so that the articles are "rumbled" over one another and expose a new surface to the plating current, thus ensuring a uniform coating on all surfaces. In the conveyer type of equipment, the articles are moved through the plating solution past the anodes by means of an endless screw or a chain conveyer on which they are hung. The conveyer with the suspended articles upon it constitutes the cathode. Usually in this method the articles after having been attached to the conveyer are carried in turn through the preliminary cleaning and washing tanks, the plating tank and the final washing baths so that no handling of the articles is necessary except to place them on and remove them from the conveyer.

For coating wire and wire products such as wire screen cloth, the process is also a continuous one. The wire passes in turn through the pickling and washing tanks, the plating bath and then through the final washing tank. As many as thirty wires, each from a separate reel, are passed through the bath simultaneously and in order to permit the wire to be pulled through at a relatively rapid rate the plating tank must be made very long. Tanks as long as 150 feet are used [B 95]. Wire screen cloth is coated in an entirely analogous manner although it is often found advantageous to pass the screen up and down over a series of rollers in order to permit the use of smaller plating tanks. In all the above cases, for any given set of plating conditions the thickness of the coating is determined by the length of time the articles are in the plating bath.

Plating Baths.

The solutions commonly used in zinc plating are either a slightly acidified zinc sulfate or an alkaline cyanide solution. Addition agents of various kinds are often used for producing fine grained smooth deposits. According to a recent investigation by Frölich, however [B 199], more care should be exercised in the choice of addition agents than is generally supposed. He has shown that organic colloidal substances such as glue or gelatin do not improve the character of deposits made from the commonly used acid sulfate or chloride baths. The cyanide bath has decided advantages over the sulfate especially in its throwing power [B 190] and is therefore preferred for plating threaded or machined articles or those having an irregular shape or rather deeply recessed parts. The deposit obtained from the cyanide bath is quite uniformly distributed over the surface of the plated article even though the surface to be covered is rather irregular in contour.

For the large mill installations, as for wire and wire products, the sulfate bath is used practically exclusively.

Properties of Electroplated Zinc Coatings.

An electroplated zinc coating is essentially pure zinc and, unlike coatings made by hot-dipping or by cementation, contains no layers of alloyed iron. Schwartz [B 191] has reported the average composition of such coatings to be 99.85 to 99.90 per cent zinc with traces of copper, lead and iron together with some inclusions, the nature of which depends on the addition agents in the plating bath. The metallic impurities will, of course, vary principally according to the composition of the anodes used. Hydrogen, to the extent of 0.055 per cent was reported by Schwartz in freshly deposited coatings but was driven off by heating at 105°–110° C.

Electroplated coatings will withstand severe bending or other mechanical deformation very much better than other types of zinc coatings of the same thickness. According to results of some adherence tests by Burgess [B 3] in which the force required to separate the coating from the base metal by means of a brass disc soldered to the surface was measured, the adherence of electroplated coatings was found to be nearly twice as great as for zinc coatings made by the dipping process. The superior mechanical properties of zinc-plated coatings are, however, more properly to be attributed to the absence of the alloy layers than to greater adherence to the base metal. One interesting application of the superior mechanical properties of electroplated zinc coatings is the use of zinc-plated rivets for the fabrication of metal culverts and similar constructions. Even after the riveting operation, enough of the coating adheres to the head of the rivet so as to afford considerable protection against corrosion in service later.

Structure of Electroplated Zinc Coatings.

The structure of electroplated zinc coatings is relatively very simple. They consist of a layer of zinc, no alloy layer being present. The crystal size and form may vary within very wide limits according to the conditions of deposition. The first requirement, of course, in any electroplating operation is that the deposited metal shall form a continuous coating. The micrographs in Figure 36 [B 200] illustrate how, with very low current density, zinc will be deposited from either a sulfate or a cyanide bath in the form of numerous isolated nodules rather than as a continuous layer. It will be noticed that the deposit from the cyanide solution was decidedly better, however, even with the low

current density employed, than that from a sulfate solution deposited under similar conditions.

Zinc coatings deposited from cyanide solutions normally have a very fine grain structure and a very smooth surface which is almost porcelain-like in its appearance. The differences shown in Figure 37 are typical of zinc coatings deposited from the two common solutions, cyanide and sulfate. By the use of addition agents usually of a colloid nature, in

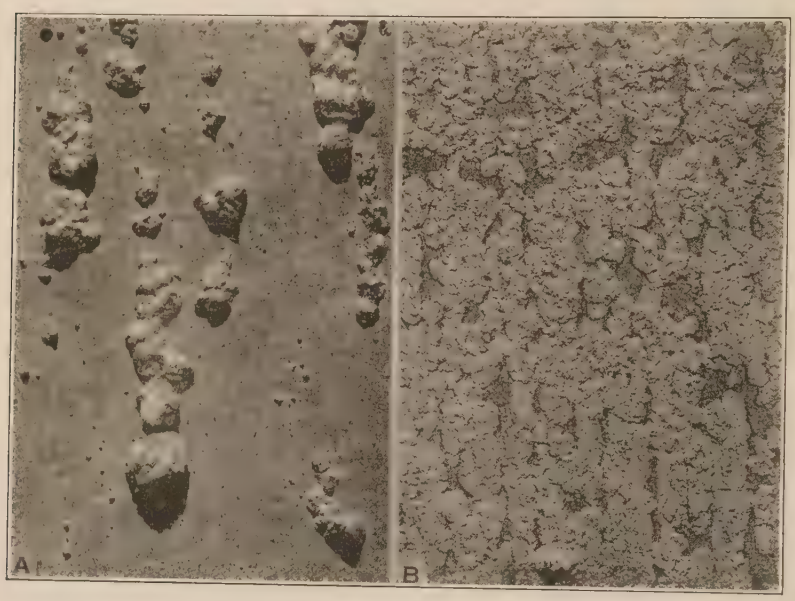

FIG. 36. Surface of a steel sheet plated with zinc at low current density, × 10. [B 200.]

Approximately 0.04 amp./dm² .37 amp./sq. ft.) was used in both cases.
A, An acid zinc sulfate solution was used.
B. A cyanide solution was used. Note that the surface was much more nearly covered than in *A*.

the plating bath, the structure and appearance of a zinc coating made by the use of zinc sulfate baths can be made as smooth and fine-grained as those from a cyanide bath. This is illustrated by Figure 38.

From the viewpoint of corrosion-resistance, such features as a rough uneven surface or a coarse-grained microstructure are, in themselves, practically negligible. Coatings showing these features, however, as a rule are more porous, that is, not so dense and impervious as fine-grained smooth deposits are. Hence failure, upon exposure to corrosive conditions, may be expected to occur in a somewhat shorter time for the rough uneven coatings. The mechanical properties of

rough, coarse-grained coatings, that is, the ability to withstand severe deformation, are inferior to those of fine-grained smooth deposits and, also, the resistance to abrasion is probably less.

Miscellaneous Zinc-coating Methods.

A method for zinc coating in which the coating material is melted, in place, on the surface of the article to be coated has been described [B 201, B 202, B 203]. The name "epicassit", from two Greek words,

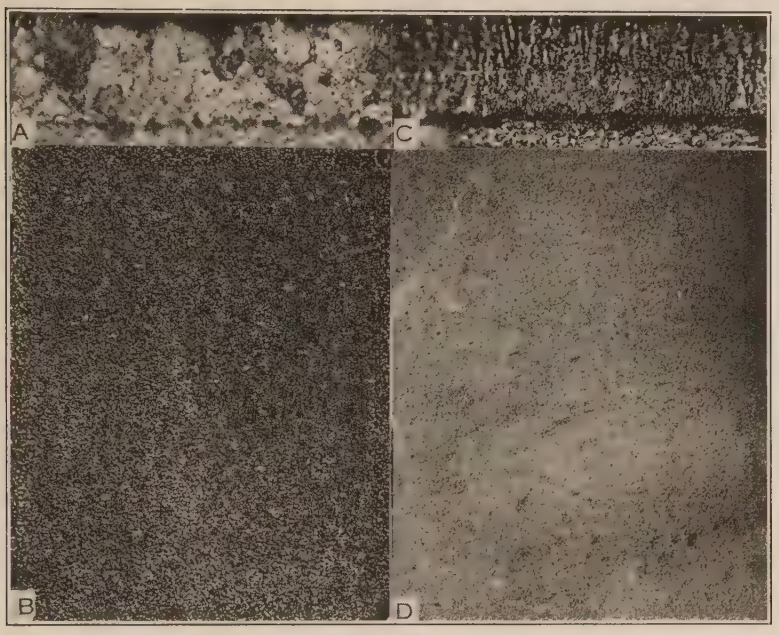

Fig. 37. Structure of a zinc coating plated from an acid-sulfate and from a cyanide bath [B 200].

A, cross section of *B*, × 500.
B, surface of a zinc coating from a sulfate bath, × 10.
C, cross section of D, × 500.
D, surface of a zinc coating from a cyanide bath, × 10.

meaning "to burn upon", was used as descriptive of the process. The zinc in the form of powder, as free from oxide as practicable, mixed into a paste with oil containing some fluxing substance is applied to the surface and then heated by a torch until the metal melts. Under the influence of the flux used, which is usually zinc chloride, the molten metal spreads evenly over the heated surface. It has been recommended especially for repair work, either for covering defective spots initially present in the coating or for coating areas from which the coating has

peeled as a result of deformation incidental to fabricating operations. It is also useful for recoating areas upon which stripping tests have been made for determination of the weight of coating. The method

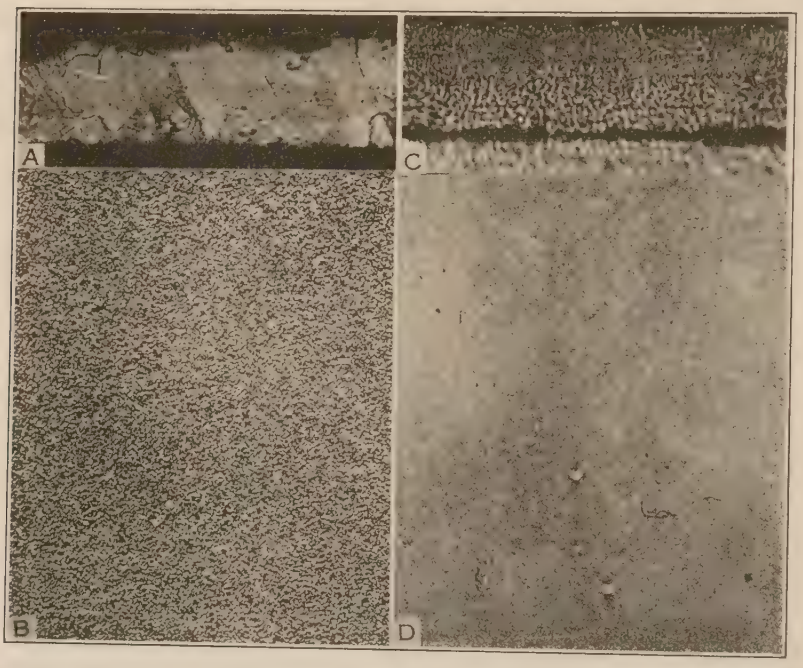

FIG. 38. Effect of an "addition agent" on the structure of a zinc coating [B 200].
A, cross section of *B*, × 500.
B, surface of a coating from an acid-sulfate bath, with no additions, × 10.
C, cross section of *D*, × 500.
D, surface of a zinc coating from the same bath as *A* after the addition of dextrin, × 10.

is applicable to other metals than zinc, especially tin and lead, but the applications of the method are extremely limited.

RELATIVE CORROSION RESISTANCE OF VARIOUS KINDS OF ZINC COATINGS.

Much has been written concerning the relative corrosion resistance of electroplated and other types of zinc coatings. The conclusions expressed have invariably been based upon the resistance of such coatings to laboratory corrosion tests such as a series of immersions in dilute sulfuric acid with determination of the loss of zinc for each immersion [B 3]. Copper sulfate solutions (Preece test) have also been used. From the results of stripping tests as well as such accelerated tests as

immersion in distilled water or dilute sodium chloride solution [B 24], the conclusion has been drawn that electroplated zinc coatings are decidedly superior in their corrosion resistance to other types. Results of comprehensive atmospheric exposure tests to verify such conclusions are not available. It is generally recognized, however, that the life of a metal, coated or uncoated, when exposed to atmospheric corrosion is dependent, to a very large extent, upon the possible formation, from the products of initial corrosion, of an adherent protective layer which inhibits or retards subsequent corrosion. Whether an electroplated zinc coating has a greater tendency toward the formation of such a protective film than has a hot-dipped zinc coating, for example, is still undecided. In case the coating is perforated and the base metal exposed, however, there would seem to be no doubt whatever that the pure zinc coating, on account of its higher solution pressure, would be somewhat more effective in protecting the exposed metal from corrosion than zinc contaminated with other metals such as iron.

Wernlund [B 193] has reported that zinc-plated coatings containing an appreciable amount of mercury are more resistant to corrosion than similar zinc-plated coatings without mercury. Such coatings can be deposited from a cyanide bath by using anodes containing mercury. The mercury content must not be allowed to increase above approximately 2 per cent, since the mechanical properties of the coatings are adversely affected by a mercury content higher than this. The results given by Wernlund (Table 7) show the relative corrosion resistance of zinc-plated coatings made in different ways.

TABLE 7.—RELATIVE CORROSION RESISTANCE OF ZINC COATINGS FROM DIFFERENT PLATING BATHS [B 193].

Plating Conditions	Relative Corrosion Resistance[1]				
	Sodium Chloride Spray			Atmospheric Exposure	
	Sheet	Wire Cloth	Auto. Rims	Wire	Auto. Rims
Cyanide bath Hg-Zn anodes	100	100	100	100	100
Cyanide bath, ordinary Zn anodes	80	84	85	79	81
Zinc sulfate bath	36	37	21.5	39	8

[1] The material showing the best corrosion resistance in each case was given a rating of 100, the others of each class were rated on the same scale.

It is well recognized that the zinc cyanide plating baths are superior to the sulfate bath in throwing power. In addition, some investigators [M 22] have concluded that even on flat surfaces the coating deposited

from a cyanide bath is superior to a similar coating from a sulfate bath in its resistance to accelerated corrosion tests. This is shown by the results in Table 8.

TABLE 8.—RESULTS OF INTERMITTENT-IMMERSION TESTS OF ZINC-PLATED ARTICLES, IN AMMONIUM CHLORIDE SOLUTION [M 22].

Plating Bath Used for the Coating	Weight of Coating[1]	Average Number of Immersions Before Appearance of Rust		
		Deep-drawn Part	Angled Part	Flat Surface
	Mg./dm.[2]			
Cyanide	155	21	97	195
Cyanide	620	168	345	632
Sulfate	775	10	27	559

[1] Weight of coating, oz./per sq. ft.; 0.05, 0.20, and 0.25.

Wernlund also concluded from his data [B 187] that there is a decided difference in the properties of the two types of deposit. According to his results a coating of 0.1 ounce of zinc per square foot plated from a cyanide solution is equivalent to one of 0.2 ounce per square foot plated from a sulfate bath in its corrosion resistance as shown by accelerated corrosion tests. Further information on this point is needed.

A decided advantage in the use of zinc-plating over other zinc-coating methods lies in the fact that the mechanical properties of the base metal are not affected as they are in processes which necessitate the heating of the material during the coating operation. It is possible, therefore, to zinc-plate hardened and tempered steel articles without affecting the hardness. The total amount of such hardened and tempered steel articles requiring plating is, however, very small.

On the other hand, zinc-plated iron and steel are sometimes embrittled somewhat during the plating operation. This is to be attributed to the effect of hydrogen evolved at the cathode [B 183, B 198]. By heating the plated articles for a short time somewhat above 100° C. (212° F.) the effect disappears, most of the "cathodic" hydrogen being driven off at a low temperature.

Zinc coatings even when polished do not possess a very pleasing appearance. For many purposes, therefore, they are not desirable. Methods for improving the ornamental appearance of the coating without sacrificing its protective value have been proposed. Nickel plating over the zinc has been used considerably. According to Blum and Hogaboom [N 21] this practice is not to be recommended. The applica-

tion of suitable air-drying or baking enamels on the zinc is suggested by them as the most satisfactory means for improving the appearance of zinc-plated articles.

Until adequate and reliable information concerning the life of zinc coatings under known service conditions is available, preferably as a result of atmospheric exposure tests of such materials, any recommendation concerning the proper type and weight of coating for any given service will always be subject to question. The following recommendations by Hubbell and Finkeldey [B 150] are about as definite as our present knowledge of the life of zinc coatings will justify:—

"1. For all outdoor and severe indoor service use only materials heavily galvanized by the hot dip process. Sheet and wire products should be purchased under specification to secure heavy enough coatings to give long life. All articles whose manufacture requires severe deformation should be galvanized after fabrication.

"2. For semi-protected outdoor and equivalent indoor exposures sherardized or lightweight hot-dipped coatings are satisfactory. Sherardizing is especially adopted to small castings, fittings, bolts and nuts.

"3. For indoor exposures under normal conditions electrogalvanized coatings will be satisfactory. The process is used chiefly to coat small working parts of machines and similar apparatus requiring protection from rusting for their proper mechanical performance."

Numerous instances can be cited, however, of the apparently successful usage of zinc-plated materials for semi-protected outdoor service.

Hubbell and Finkeldey have also, on the basis of existing data, given an estimate of the probable life of galvanized products when exposed to the weather in the unpainted condition (Table 9).

TABLE 9.—ESTIMATED LIFE OF UNPAINTED ZINC-COATED PRODUCTS EXPOSED TO THE WEATHER [B 150].

Class of Material	Life in Years Under Atmospheric Conditions			
	Rural	Sea Coast	Semi-industrial	Heavy Industrial
Commercial rolled zinc sheet or strip 0.020″ thick	50–75	50	20–30	10–15
Galvanized product, 1.25 oz. coating per sq. ft. of surface	30–35	20–25	15–20	8–10
Galvanized product, 1.0 oz. per sq. ft. of surface	20–25	15	10–15	6– 8
Galvanized product, 0.6 oz. per sq. ft. of surface	8–10	5– 8	5	3– 5
Galvanized product, 0.2 to 0.3 oz. per sq. ft. of surface	3– 4	2– 3	1– 2	1

Chapter 8.

Tin Coatings.

In some respects tin is an almost ideal coating metal. It is resistant to ordinary atmospheric corrosive attack and can be applied as an extremely thin coating very uniformly distributed over the surface. Tinned sheet metal can be very severely deformed without any material damage to the coating being done, hence it is admirable material for forming operations. So long as the coating is intact, it gives excellent protection to the metal beneath from corrosion, but it affords no protection in an electrochemical way after the underlying metal has been exposed such as a zinc coating does. Great quantities of tin-plate are used in the canning industry since it lends itself admirably to soldering operations and has no toxic effect upon foodstuffs in contact with it.

The manufacture of tin-plate is a very important industry. Very great quantities of this material are used commercially, the use being dependent upon other properties than the effectiveness of a tin coating as a protection against severe corrosion.

Hot-dipped Tin Coatings (Tin-plate).

Historical.

Metallic tin has been used for many centuries. In the form of its alloy with copper (bronze) it was known before the dawn of history. It appears, however, that most of the early bronze was not made directly from the constituent metals, copper and tin. Although doubt has been expressed [C 16] concerning some of the early Biblical and other references, usually translated as referring to tin, there can be no doubt that the metal had become an important article of commerce by the first century, B.C. The main sources of supply for the Mediterranean countries were in Spain and Cornwall in England. Flower [C 4] states that the tin trade of the Phoenicians was well developed by the year 300 B.C., while Hoover [C 17] places the beginning of this trade much earlier, 1500 to 100 B.C.

The coating of copper vessels with tin was well known to the Romans and considerable skill seems to have been attained by them in this art. The Romans have also been credited with the tinning of cast-iron cook-

ing utensils by Flower [C 2, C 4] who states that such articles date from the time of Pliny, A.D. 23. According to Goodale [C 43], such evidence as is available indicates that the coating as carried out by the Romans was done by immersion in a bath of molten tin. It seems reasonable to believe, however, that the much simpler process of tinning by applying the metal to the surface of the heated article was also employed.

The coating of sheet iron with tin is of much more recent origin. Its beginning is obscure but it is an established fact that the art was well known in Bohemia by the year 1620. It apparently had been practiced there for generations prior to this date, the discovery of tin in Bohemia having been made about the middle of the thirteenth century. About the year 1620, the manufacture of tinned iron sheets was begun in Saxony. The story is told that the secret of the art was stolen for the Duke of Saxony by a Roman priest disguised as a Lutheran. By 1665, Dresden had become a flourishing center for the manufacture of this material.

The introduction of tin-plate manufacturing into England is the result of the efforts of Andrew Yarranton, who, during a period of depression in the metal industry in England, particularly as relating to tin, visited Dresden for the express purpose of becoming familiar with the making of tin-plate. The party was well received in Dresden and no efforts were made to conceal any of the operations. Yarranton returned to England with the information sought and shortly afterwards made preparations for starting the industry at Pontypool in southwestern England. The establishment of the industry was a slow process and extended over a number of years and was finally discontinued because of the granting of a patent for the process to a rival who had influence at court. Not until 1720 was anything really constructive done when Hanbury took up the project again at Pontypool, this time with success. Once started, the industry increased rapidly, especially after a method for producing the iron sheets by rolling instead of hammering them by hand was developed in 1728, and the South Wales district became the center for the production of practically all of the world's supply of tin-plate, a position which it retained until late in the 19th century.

The manufacture of tin-plate in the United States is of very recent date. Not until the McKinley tariff act of 1890 was in force was any headway made. This act imposed a heavy duty (2.2 cents per pound) on tin-plate and, by shutting out the foreign product, assured the success of the domestic manufacture of this material although later tariff acts reduced the duty somewhat.

Outline of the Process

As in the analogous case of zinc coating, the application of a tin coating to a material such as sheet steel constitutes only a small part of the total work required in preparing such material. Although there are characteristic differences in preparing the sheets in the zinc-coating and tin-coating industries, the essentials are the same. Careful cleaning by acid pickling is very important. In the tinning industry, this is carried out in two stages: the first, which is termed "black pickling", is carried out on the black sheets in sulfuric acid (approximately 4%) which is kept hot with steam. After the annealing, cold rolling and second annealing operations which follow the first pickling, the sheets are given the "white pickling" in dilute sulfuric acid (2%) and after washing are ready for the tinning operation.

Hand Dipping.

The old process for making tin-plate by hand dipping is of interest. The sheets were cleaned by scouring with sand and water and by being immersed in sour barley water for several days. The use of sulfuric acid for pickling dates only from the early part of the nineteenth century. The sheets, after being cleaned, were immersed in a bath of hot grease prior to immersion in the molten tin. Tallow, which was used in the early days and is used to a limited extent today in hand dipping, was replaced later by palm oil which is still widely used for this purpose. From the grease pot the sheets were lowered one by one into the molten tin which was kept covered with a thick layer of the grease in order to prevent oxidation. Upon removal from the first tin bath, the sheets were brushed with a hemp brush and again immersed in a second tin bath usually of somewhat higher purity and maintained at a somewhat lower temperature than the first, and finally in a third tin bath of highest purity. Close regulation of the amount of tin carried by the sheet was not possible although the workmen became very adept in obtaining very uniform distribution of the coating over the surface of the sheet. After the coating had solidified, the sheets were rubbed free from most of the oil by means of bran or a similar substance and then "dusted" with a sheep fleece to give a high luster. Sheets coated in this manner always had a very heavy coating as compared with the present commercial "coke" plate.

The present-day hand-dipping method for the tinning of small irregularly shaped castings and for the tinning of articles cut or stamped out of tin-plate or plain "black" sheet steel, such as kitchen utensils, does not differ essentially from the old hand-dipping method. The

retinning of articles is also done in essentially the same manner. Considerable difficulty is often experienced in tinning castings by hand dipping, primarily on account of an improperly cleaned surface. The first cleaning is often done with hydrofluoric acid and sometimes sand blasting is employed. After this, the casting is pickled and the resulting film of graphite must then be carefully rubbed off. Following this, a treatment with a copper solution so as to give a film of precipitated copper is often recommended [C 39, C 83]. The article is then immersed in the molten tin, the flux commonly used being zinc chloride. Iron castings which have been given an annealing treatment somewhat akin to the treatment used for producing malleable castings, so that surface decarbonization has been brought about, can be tinned, as a rule, very much more readily than ordinary castings.

Mechanical Dipping.

A marked advance in the tinning process was the invention, about 1863, by Morewood and, independently, by Saunders and Piper, of a device for passing the sheets as they came from the bath through a set of rolls located in the oil layer above the tin. The rolls worked rather closely against each other so that the molten tin was distributed uniformly over the surface.

The use of zinc chloride as a flux for treating the sheets prior to immersion in the tin accompanied and, to some extent, made possible the use of the single bath of tin instead of the several separate baths used in the early days. The single-bath method is used today almost exclusively for tinning when carried out mechanically, although the bath is usually divided into two compartments. Figure 39 is a section of a tinning pot used early in the industry and shows the arrangement of the essential features, flux, molten tin bath, palm-oil layer and rolls. The sheets, after being cleaned, were fed by hand one at a time through the flux into the tin and then raised by the lever vertically so as to be caught by the rolls and carried upward and out of the pot. This method in principle, is still used, though to a very limited extent [C 37, C 75], for the production of heavily coated tin-plate. It is not suitable for very long sheets which are apt to buckle and bend when raised from the lower edge, nor is the method a rapid one.

Figure 40 shows a section of a tin pot in current use for the mechanical tinning of the grade of tin-plate commonly termed "coke plate" [C 77]. Such a pot contains from 5000 to 10,000 pounds of tin. The apparatus is a well known and approved type of tinning machine.

The sheets after being cleaned are, by means of the rolls and guides at the right, passed through the zinc chloride flux layer into the molten

tin. The molten metal in the first compartment of the cast-iron container is generally kept at a somewhat higher temperature than that in the second. The machine is usually wide enough so as to permit two or more sheets to pass through side by side simultaneously. The sheet is guided through the tin bath by the curved guides shown, and by means of the rolls is passed upward through the oil layer. The oil keeps the tin coating on the sheet molten long enough so as to aid in

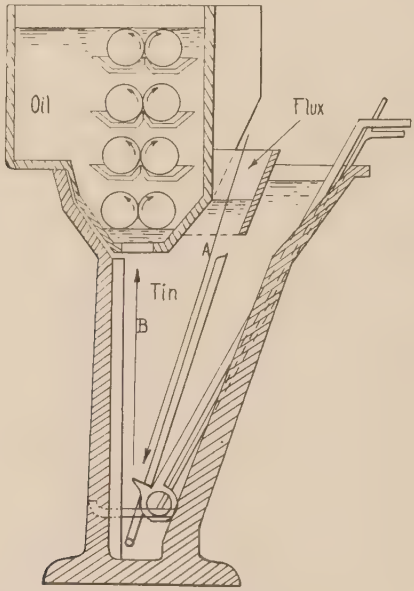

FIG. 39. Early form of tinning machine [A 13]. The arrows indicate how the sheet is passed through the tin and oil baths. The pans beneath the exit rolls contain molten tin to aid in forming uniform and heavy coatings.

obtaining a layer as uniform in thickness as is possible. It also aids in giving luster by preventing any superficial surface oxidation.

The machine process as just described is not depended upon for the production of heavily coated tin-plate ("charcoal plate") except perhaps for rather light-gage sheets. For charcoal plate, a "combination pot" is often used [C 75]. In this process the sheet is first dipped mechanically in a manner analogous to that described above, after which it is dipped by hand in a pot of pure tin maintained at a rather low temperature, then passed between rolls in the palm-oil bath, whereby the relatively heavy coating of tin is uniformly distributed over the surface.

The tin-coated sheets always carry with them as they leave the oil

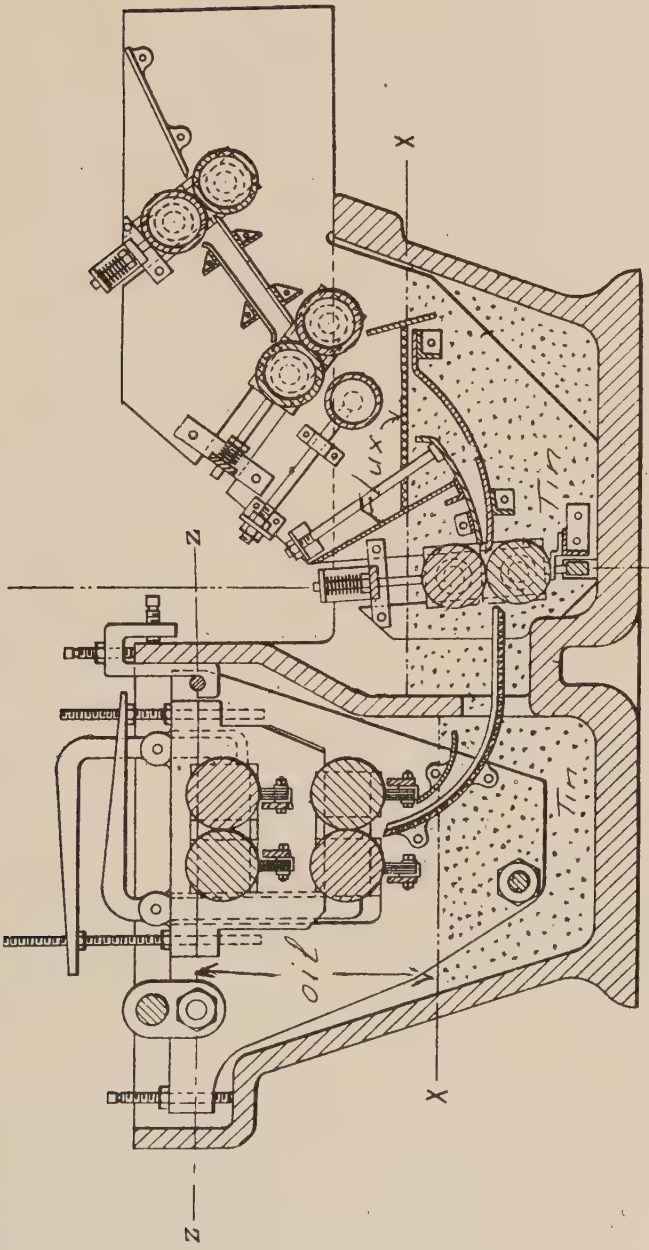

FIG. 40. Section of the "tin pot" of a modern tinning machine [C 77].

bath a film of oil. The greater part of this must be removed by rubbing with some substance such as bran or middlings. The sheets are then cleaned so as to give a high luster although often this cleaning is almost simultaneous with the "branning" for the removal of the oil. Unless the sheets are cleaned chemically, for example, by immersion in an alkaline solution, as is sometimes done for special products, all grades of tin-plate retain some oil on the surface. This serves a useful purpose, however, in retarding the initial corrosion of the sheet especially during storage and shipment.

Aside from the tinning of copper wire very little wire is tinned. The process is carried out in a manner quite similar to the zinc-coating of wire.

The tin used in the manufacture of tin-plate is of high grade and no attempt is made to use any additions as is not infrequently done in the zinc-coating industry. The addition of aluminum, for example, would be expected to be very detrimental since sheet tin containing traces of aluminum soon becomes so brittle as a result of corrosive attack [C 54] that it can be broken up into tiny fragments by the fingers. According to Maass [C 73] the presence of several per cent of zinc in a tin coating improves its corrosion resistance, 5 to 10 per cent of bismuth makes a tin coating much whiter and brighter, and iron to the extent of 0.5 to 1.5 per cent increases the hardness and wear-resistance. Such additions, however, if used at all are for very special products and not for commercial tin-plate.

The "spangle" effect which is so pronounced in zinc coatings is entirely lacking in tin coatings, ordinarily. Occasionally, tin-plate has a spangled or mottled appearance somewhat similar to that seen on terne-plate (p. 176). Such material, like "gray" galvanized sheets, is not so readily salable as the regular product, however. The crystalline pattern of tin coating can be readily developed by dipping the coated article in dilute hydrochloric acid and this is sometimes done for ornamental effects. Such an etch-pattern is often very pronounced on the inner surface of tin cans in which certain food products have been preserved.

Temperature and Other Bath Conditions

As in the case of zinc-coating, the temperature control of the tin bath is of very considerable importance. Collins and Clarke state that 315° C. (600° F.) is the usual working temperature of the tin bath, while that of the palm-oil layer is 240° to 250° C. When the bath consists of two compartments the temperature of the tin in the first one is kept considerably higher than in the second. Camp and Francis [C 75]

give 300° C (570° F.) as a good working temperature for the tin in the first compartment and 245° C. (475° F.) for the temperature of the oil. The need for a somewhat lower temperature in the second compartment arises from the fact that the palm oil is in direct contact with the tin here. If the oil becomes too hot, it polymerizes and loses its power to keep the tin clean and is also carried off in undue amounts on the tinned surface of the sheets as they leave the oil bath.

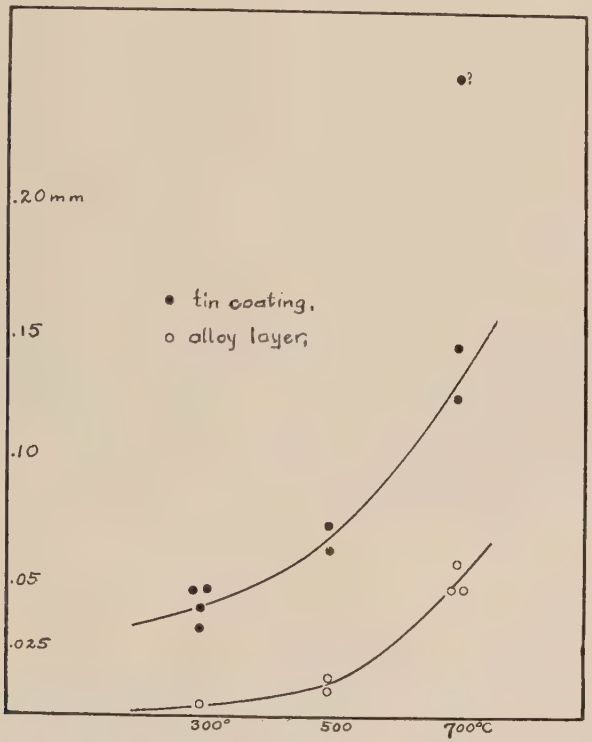

FIG. 41. Effect of the temperature of the tin bath upon the thickness of coating and upon the alloying between base and coating [C 34].

Pronounced alloying between the tin and the iron base is an undesirable feature and is sometimes given as a reason for maintaining the temperature of the tin bath within certain limits. As a matter of fact, however, the sheet is in the molten tin for such a short time that the alloying action is extremely slight.

Figure 41 summarizes the results obtained by Mayer [C 34] on the effect of temperature on the thickness of tin coating and of alloy formation. The tinning of the sheets was carried out on a small scale by

hand dipping. They were allowed to remain in the molten tin at the temperature indicated for one-half hour and then cooled to 300° C. and removed from the bath without any attempt to roll them or regulate the thickness of the coating in any way. The conditions are, admittedly, not at all those of commercial tinning but information along this line is almost entirely lacking in the technical literature. The data in Table 10 on the amount of alloy formed in tinning operations carried out on a commercial scale show that the rate of alloy formation, even under favorable conditions, is very slow.

In addition to the temperature of the bath, the speed at which the sheet is passed through the molten tin in commercial practice is an important factor in determining the amount of tin used in coating a unit area of sheet, or the "yield" as it is known in the mill. According to Davis [C 77] a speed of 100 to 120 inches per minute through the tin pot used to be considered the maximum to be used in the tinning of coke plate. By the methods now in use, however, the tinning is done with the sheets traveling at a speed considerably higher than this.

The thickness of a tin coating is also dependent upon the character of the surface of the sheet, particularly its condition with respect to the degree of pickling received. A sheet roughened by "over-pickling" takes up considerably more tin than a properly pickled sheet and it is also hard to impart a satisfactory luster to such sheets. The adjustment of the exit rolls, that is, their grip on the sheet, is an important factor in determining the uniformity of the coating.

By-products.

As in the case of the zinc-coating of steel, an appreciable amount of the molten tin alloys with the iron. This alloy consists to a large extent of the compound $FeSn_2$. This alloy, known in the mill as "heavy metal" or "scruff", collects in the lower part of the tin pot and is removed at intervals and smelted for the tin which it contains. The term "scruff" is also applied to the scum of tin oxide and burnt oil together with various foreign matters which float on the surface of the bath. Other sources of loss of tin are in the spent flux, or "flux scruff", and in the waste oil. This is burnt to recover the tin it carries. On account of the value of the tin contained very considerable care is taken in the recovery of all of these products. Figure 42 shows the structure of a sample of tin scruff which showed upon analysis an iron content of 2.95 per cent.

The middlings used in the removal of the palm oil from the plate after tinning can be used for only a relatively short time. The amount of adsorbed oil determines the limit of usefulness of the material. No

attempt is made to recover the oil since there is a ready market for the material as cattle food.

Substitute for Palm Oil.

Collins and Clark [C 42] have given results of an investigation as to the use of possible substitutes for the palm oil used in the tinning process. It is stated that from 5000 to 10,000 tons of this oil are imported annually for use in this industry alone. Of the oils investi-

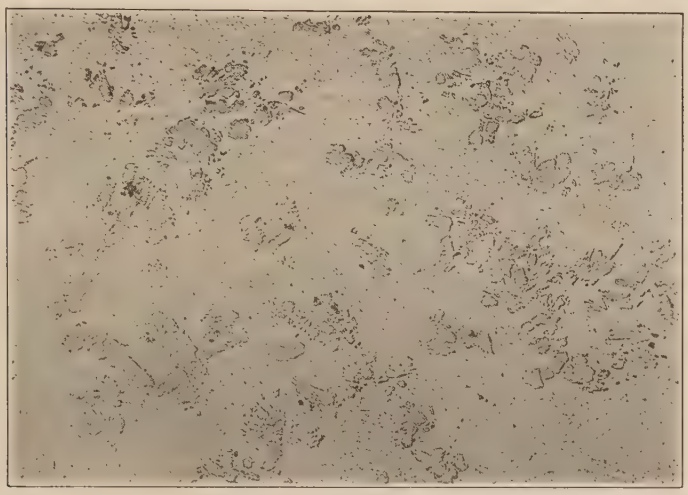

Fig. 42. Microstructure of tin "scruff," × 100. The alloy has an iron content of 2.95 per cent. The compound, $FeSn_2$, occurs as nodules embedded in a soft matrix which is nearly pure tin.

gated, they reported hydrogenated cotton-seed oil as the best. They concluded as a result of their investigation, which was tried out on a full-sized mill scale for twelve weeks, that the operation of a tinning pot with the hydrogenated cotton-seed oil was somewhat better than with the palm oil. The consumption of the oil was distinctly less although there was no saving in the amount of tin used. With the present organization of the industry, however, it was concluded that no material saving would be effected by changing from one oil to the other, but the practicability of the change in time of any national emergency was emphasized.

Structure of Tin Coatings.

At least a slight alloying action between the base metal and the coating metal must occur in order for the hot-dipping process to be a success. It is to be expected, therefore, that a hot-dipped tin coating on

iron will be somewhat analogous in its structure to that on a zinc-dipped iron sheet. The coating on tin-plate is extremely thin, however, the thickness of the coating corresponding to a weight of tin of one pound per "base box" (p. 138) being only 0.00015 centimeter or 0.000059 inch. In the ordinary coke plate the amount of tin per base box is 1.5 pound according to Davis [C 77], although some [C 75] place it somewhat above 2 pounds per base box. The value varies, however, and as shown in Table 9 may be very considerably lower than the value set by Davis.

The alloy layer in the coating of commercial tin-plate is extremely attenuated and often no evidence of it can be detected in metallographic sections of the coated sheet. Its presence can usually be demonstrated, however, by very careful polishing and etching of a slightly bent surface of the sheet. The alloy layer appears as a bluish film underlying the layer of tin which comprises the body of the coating.

Kohman [C 86] has devised a method for determining the amount of alloyed tin in a tin coating. The unalloyed tin in a tin coating dissolves readily when the sample of tin-plate is immersed in a hot solution of sodium plumbite; the iron-tin alloy does not dissolve nearly so easily. Results obtained by the use of this method on commercial and special grades of tin-plate are summarized in Table 10. It will be

TABLE 10.—WEIGHT OF COATING ON TIN-PLATE[1] [C 86].

Specimen	Material	Weight of Coating	Unalloyed Tin		Alloyed Tin	
		Lbs./ Base Box	Lbs./ Base Box	Per Cent of Coating	Lbs./ Base Box	Per Cent of Coating
1	Commercial coke plate	1.19	.98	82.5	.21	17.5
2	Commercial charcoal plate	3.82	3.62	94.8	.20	5.2
	Special plate[2]					
3	1 min. at 600° F.	1.24	.96	77.5	.28	22.5
4	5 " " 600° F.	1.22	.82	67.3	.40	32.7
5	10 " " 600° F.	1.39	.88	63.4	.51	36.6
6	30 " " 600° F.	1.82	1.08	59.4	.74	40.6
7	60 " " 600° F.	2.55	1.56	61.2	.99	38.8
8	30 " " 500° F.	1.49	1.03	69.1	.46	30.8
9	30 " " 550° F.	1.47	.90	61.2	.57	38.8
10	30 " " 650° F.	2.25	1.35	60.0	.90	40.0

[1] The unalloyed tin was taken as that which was readily soluble in a hot solution of sodium plumbite.

[2] All of the special tin-plate was held in the molten tin for the indicated time at the temperature given. It was then run through the machine in the same manner as coke plate is.

noted from these results that the amount of alloyed tin in the coating on coke plate was found to be the same as on charcoal plate. The percentage of alloy in the tin coating on coke plate was readily increased several fold by keeping the plate immersed in the tin bath prior to running it through the tinning machine.

Not many investigators have studied the iron-tin system of alloys. The recent work of Wever and Reinecken [C 76], however, has furnished answers to most of the questions left unanswered after the early work of Isaac and Tammann [C 10, C 15]. The portion of the diagram of Wever and Reinecken having a bearing on the structure of tin coatings on iron is given in Figure 43. These investigators concluded that iron and tin are completely miscible in the liquid state whereas former investigators had stated that they were only partially so. As shown in Figure 43, solidification of the tin-rich alloys begins by the crystallization of a compound $FeSn_3$ (41.3% tin) out of the melt. At 890° C. (1635° F.) a peritectic reaction between this compound and the molten phase gives rise to the compound $FeSn_2$ (81% tin). For alloys with a tin content greater than 81 per cent, solidification is not complete until a temperature slightly below that of pure tin (231.9° C.) is reached. The exact temperature has not been reported. Wever and Reinecken attributed the heat changes, shown in the diagram at 780°, 755°, and 490 °C., to "polymorphic transformations" in the compound $FeSn_2$. At ordinary temperatures, tin-iron alloys with a tin content between 100 and 81 per cent, consist of a matrix of a solid solution of a very small amount of iron in tin, embedded in which are crystals of the second phase, the compound $FeSn_2$. No reliable information as to the limit of solubility of iron in tin is available. It is only a few hundredths of a per cent at the most, however. It may be concluded then that a hot-dipped tin coating, as in tin-plate, has essentially the same general type of structure as a hot-dipped zinc coating, that is, an alloy layer immediately adjacent to the iron base and an outer one of tin covering this alloy layer. On account of the rather low temperature used in tinning relative to the temperature at which the compound $FeSn_2$ is readily formed, as well as the very short period the sheet is exposed to the action of the tin, the alloy layer in the coating on tin-plate is extremely attenuated.

The compounds of tin and iron bear the same general electrochemical relation toward iron that tin does [C 15], that is, they serve as cathode and the iron as anode when the two are in contact and wet with an electrolyte. The effect of the alloyed tin upon the service behavior of the coated iron with respect to corrosion is therefore of no practical

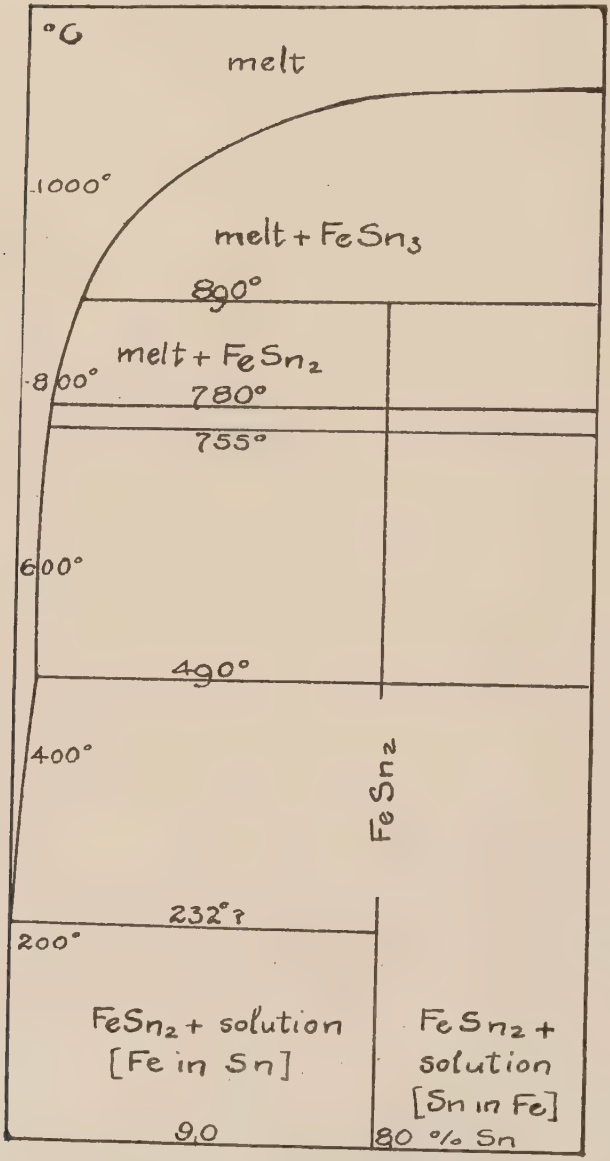

FIG. 43. Portion of the equilibrium diagram of the iron-tin alloy system [C 76].

concern since pure tin itself affords no electrochemical protection to iron against corrosive attack. Since the alloy layer is always extremely thin the possibility of the mechanical properties of the coating being adversely affected by it is a very remote one.

Defects in Tin-plate.

In the inspection of tin-plate many of the defects which may be a cause for rejection are mechanical in origin, such as round corners, under-sized sheets, ragged edges, "pinchers" or rolling defects, and untinned spots caused by improper cleaning and similar causes. In the inspection of the finished plates, which is a "100-per cent" inspection, the sheets are classed as (*a*) primes, (*b*) seconds, (*c*) menders, and (*d*) waste. The "prime" sheet is not a perfect sheet, but in general is as good as can be made by present means for the particular grade of plate under consideration. The "menders" are sheets which by being retreated, usually by redipping in the molten tin, after a little cleaning, can be improved and put into class *a* or *b*; the "waste" is, as the name implies, more or less of a loss although, in the form of strips and other small pieces, much of it is salable. The "seconds" were formerly known under the name "wasters", a term often not clearly understood by the purchaser. A second is a sheet which because of certain defects, usually of limited extent, requires that extra care be taken in its usage. For can making, for example, if a second has only a ragged edge it is for all practical purposes as good as a prime sheet. If it contains a number of bare spots, the part remaining after discarding the bare areas is essentially the same as the first-class sheet. For some uses, however, in which an entire sheet must be used, second sheets cannot be considered at all.

According to Davis [C 77], it is well known among operators of tinning plants that if a sheet is left too long in the tin bath, black spots to which the tin does not adhere are formed on the surface of the sheet. The results of experiments by Kohman, however, in which sheets were allowed to remain in the bath of molten tin for periods varying from 1 to 60 minutes (Table 10) indicate that this defect is by no means a common one, especially for the conditions under which tinning is usually carried out.

The blistering of tin-plate is usually attributed to hydrogen absorbed by the steel in the pickling operation. The defect is one of the steel sheet rather than of the coating, and the blister which forms is not simply a separation of the coating from the base. Practically always, the blister forms somewhat below the surface of the steel sheet [O 2].

On practically all tin-plate, as ordinarily made, the coating shows numerous minute pinholes which extend through the tin coating to the base beneath. Their presence can readily be shown by means of the ferricyanide test (p. 220) or by allowing the sheet to rust slightly.

Microscopic examination of the surface of the tin layer shows that each pinhole is really a shallow saucer-like crater, at the bottom of which the base metal may be exposed. Examination has indicated, however, that the pinhole depression may contain a tiny crystal, apparently of the iron-tin compound which reacts toward potassium ferricyanide in the same way iron does, hence all of the spots shown by the ferricyanide test are in reality not true pinholes [C 59]. The number of apparent pinholes per unit area on tin plate is not decreased with an increase in the weight of tin per unit area in the same ratio as the increase of weight of coating. Figure 64 shows the results obtained by means of the ferricyanide test on commercial coke and charcoal tin-plate. According to Maass [C 73], it is the German practice to grade tin-plate showing no more than 3 pores per square centimeter by the ferricyanide test as first class; material showing from 4 to 12 pores per square centimeter is termed slightly porous; and that having more than 12 per square centimeter is very porous. When it is remembered how very thin the layer of tin is, it is somewhat surprising that the coating is as continuous as it is. Guertler [C 15] cites this feature, the porosity of tin coatings, as the most important field for research in the entire tinning industry.

The occurrence of pinholes in tin coatings has recently been reported by the *Materialprüfungsamt*, Berlin [C 85], as being caused by the evolution of hydrogen retained in the iron after the pickling operations. According to the explanation advanced, the hydrogen has not been completely removed before the sheet leaves the tin bath and the subsequent evolution breaks the film of molten tin and causes the formation of the pinholes. It was stated that by heating the sheets at 100° to 200° C. in order to ensure complete removal of the hydrogen before immersion in the molten tin, coatings practically entirely free from pinholes were obtained without necessitating any material increase in the weight of the tin coating on the sheet.

It is well known that tin undergoes an allotropic change at ordinary temperatures which results in a pronounced change in the properties of the metal. Above 20° C. (68° F.), the white malleable tin is the stable form; below this temperature the stable phase is the gray brittle form of the metal. Were it not for the fact that this allotropic change is a sluggish one so that tin can be cooled very considerably below 20° C. without the transformation occurring, tin would be of very little value for coating purposes or as a commercial metal in any form. As a matter of fact, the chance of the usefulness of tin as a coating metal being impaired because of this allotropic change in the metal is a very remote one, except possibly for extremely low temperatures.

Although tin coatings are relatively soft and ductile so that they withstand very severe deformation without peeling and flaking, as zinc coatings often do, the better grade of articles, such as kitchen utensils, which are often fabricated by stamping them out of tin-plate, are retinned after stamping. This not only covers any breaks in the coating resulting from stamping but also covers any defects which may initially be present. Many such articles are now stamped out of the

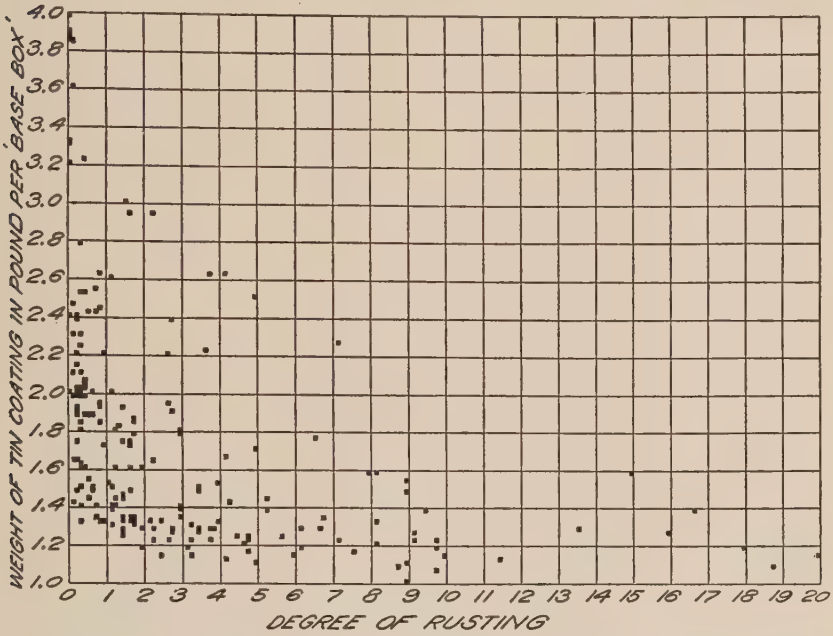

FIG. 44. Degree of rusting in weather tests of tin-plate of different weights of coating [C 59]. The degree of rusting is represented on an arbitrary scale, according to which the lower the number the smaller the amount of rust.
The exposure was for a period of three months in the vicinity of Baltimore.

uncoated or black sheet and then tinned after stamping. The degree of protection which a coating of tin gives to a steel sheet is determined almost entirely by the thickness of the coating and its continuity. The results of rusting tests of tin-plate in which the weight of coating varied from 1 to 4 pounds per base box, shown in Figure 44, illustrate this. The degree of rusting is expressed on an arbitrarily chosen scale, according to which the least amount of rusting is indicated as No. 1. It will be noted, however, that for the conditions covered by these exposure tests, which varied from 2 to 5 months in the vicinity of Baltimore, a good many of the more lightly coated sheets showed as high resistance

to rusting as the more heavily coated ones did. The committee [C 29, C 59] which carried out these tests concluded that the amount of rust which forms on tin-plate exposed to the weather is dependent upon several factors, the continuity and thickness of the coating, however, being the most important. In addition it was stated that the nature of the steel base which may be exposed through the minute perforations, the character of the surface of the steel sheet, may at times be important factors. This conclusion appears very unlikely, however, when it is remembered that tin because of its cathodic nature with respect to iron will accelerate the corrosive attack of any steel ordinarily used for commercial sheets. The amount of oil on the surface of the tin plate is of very considerable importance in determining the corrosion resistance of the material. According to Speller [A 25, p. 298] this should be taken into account when tin-plate is to be painted. It is best to clean the surface by swabbing it with a suitable solvent such as benzine before the paint is applied. Tin-plate exposed to the weather should always be kept well painted.

Tin-plate Commercial Terms.

The term "tin-plate" is, strictly speaking, incorrect. "Tinned plate" would be much more descriptive of the material and as such is used by a few [C 28]. Some use the term "tinned plate" when referring to heavy sheets when tinned. The name "tin-plate" has apparently become quite firmly fixed as a commercial term by generations of usage, however.

The weight of the coating on tin-plate is expressed as the weight of tin per "base box". The base box is essentially a unit of area, and is the equivalent of 112 sheets, 14 inches by 20 inches, that is, 31,360 square inches of sheet or 62,720 square inches of surface to be coated. The term, base box, originated in the early days of the industry, and was first used with reference to tin-plate of approximately 30 gage thickness. A base box of material of this gage weighs approximately a hundredweight, 112 pounds, a fact which is frequently, but erroneously, embodied in the present-day definition of this term. The manufacture of tin-plate is, of course, not confined to sheets of this size, but a great variety of sizes is made. Some multiple of the original "common standard" size, 10 by 14 inches, is often used especially for some of the higher-grade products. The weight of the tin coating, however, is always expressed in terms of the base box.

The names "coke" and "charcoal" plate are often used in referring to tin-plate. These terms originated in the early days of the industry

when the practice was to use sheets made from ordinary puddled iron for the common grades of tin-plate and sheets of puddled iron made with charcoal for the higher-grade plate. The original significance of the terms has been entirely lost and, as used at present, they refer in a general way to the weight of tin coating. The coke plate is a cheaper product in that it carries a much lighter coating of tin than does the charcoal plate. According to Camp and Francis [C 75], the weight of coating of tin on coke plate may vary from 1 to 2½ pounds per base box and on charcoal plate from 3 to 7 pounds per base box.

Tin-plate is made in a good many different thicknesses; it is necessary, therefore, that the sheet thickness be specified as well as the weight of coating for any particular grade of material. In designating the thickness or weight of the sheet (Table 11) various trade terms, which originated in the early days of the tin plate industry, are still used although many of these terms have lost most of their original significance. A brief résumé of the early methods used for designating the various weights of tin-plate is of interest in this connection and will serve to show the origin of many of the terms still in use [C 7].

In the early days the manufacturer made standard sizes to suit his facilities and the tinsmith cut his articles from the sheet as best he could to avoid undue waste. The chief common size, known as 1 C ("one-common") was 10 by 14 inches. Two hundred and twenty-five such sheets to a box was a hundredweight (112 pounds). To meet the requirements of some customers a sheet 25 per cent thicker but of the same dimensions was made. This was designated 1 X ("one-cross"). The next thicker sheet, designated as 1 XX, was 21 pounds heavier than the preceding one and so on through the series. As shown by the tabulation below, each added "X" after the first indicated an increase in weight of 21 pounds per box of 225 sheets. The weight of the tin coating per box remained essentially the same, however.

Designation	Size	Weight per Box of 225 Sheets. Pounds
1C	10 in. × 14 in.	112
1X	"	140
1XX	"	161
1XXX	"	182
:		:
1XXXXXX	"	245

A second standard of early days was the "common double" (CD or DC). The sheets were 12½ by 17 inches and were packed 100 to the box, the weight being 98 pounds. As in the preceding series pro-

gressive increases in sheet thickness (weight) were indicated by X as is indicated below:

Designation	Size	Weight per Box of 100 Sheets. Pounds
DC	12½ in. × 17 in.	98
DX	"	126
DXX	"	147
DXXX	"	168
		:
DXXXXXX	"	231

A third early standard size, 11 by 15 inches, 200 sheets to the box (160 pounds) was known as "common small doubles" (SDC, SDX, etc.) or "common middles". None of the terms of this series is used today. A number of terms derived from the first two series, however, for example, IC, IX, DC, etc., have a distinct commercial meaning today both in English and American practice, although the present meaning is not identical with the original one as given in the tabulations above. The weights have been reduced somewhat, about 4 per cent, and the width of the sheet doubled; thus the IC sheet of today is 14 by 20 inches and not 10 by 14 inches, the weight per base box being 107 pounds (Table 11) instead of the original 112 pounds. The present weight of the DC sheets is 139 pounds per base box of 112 sheets, 14 by 20 inches, instead of 144.5 pounds, which is the equivalent of the original weight of 98 pounds per box of 100 sheets, 12½ by 17 inches.

In order to meet the varied demands of the present day, tin-plate is made in a good many sizes and gages. Sheets thinner than No. 30 gage are usually designated by the weight per base box. The lightest-gage tin-plate is commonly known as "taggers tin". It has been the practice to name tin-plate of 30-gage thickness and heavier largely in accordance with the old-time system as indicated above. It should be noted that these designations refer to the weight of the sheet and not to the tin coating, thus, for example, two lots of IC sheets may, and very often do, carry quite different weights of tin coating. Much of the coke plate which is used largely in the manufacture of tin cans used in the canning industry is made in the larger sizes. The weights and gages of American commercial tin-plate are given in Table 11. There is decided need for simplification in the present system used for the commercial designation of tin-plate.

Tin-plate is used to a limited extent for roofing. This should not be confused with terne-plate (p. 176), a widely used roofing material, which is commonly known as "roofing tin".

TABLE 11.—WEIGHTS AND GAGES OF TIN-PLATE [C 64].

Trade Term	Nearest U.S. Standard Gage	Weight per Square Foot	Weight per Base Box (112 Sheets, 14″ × 20″)
		Pounds	Pounds
Tagger's Tin			
55-lb.	38	.253	55
60 "	37	.276	60
65 "	36	.298	65
70-lb.	35	.321	70
75 "	34	.344	75
80 "	33	.367	80
85 "	32	.390	85
90 "	31	.413	90
95 "	31	.436	95
ICL	30½	.459	100
IC	30	.491	107
118-lb.	29	.542	118
IXL	29	.588	128
IX	28	.620	135
DC	28	.638	139
2XL	27	.680	148
2X	27	.712	155
3XL	26	.771	168
3X	26	.804	175
DX	25	.827	180
4XL	25	.863	188
4X	25	.895	195
5XL	24	.955	208
D2X	24	.964	210
5X	24	.987	215
6XL	24	1.047	228
6X	23	1.079	235
D3X	23	1.102	240
7XL	23	1.139	248
7X	23	1.171	255
8XL	22	1.231	268
D4X	22	1.240	270
8X	22	1.263	275

USE OF TIN-PLATE IN THE CANNING INDUSTRY.

According to Camp and Francis [C 75] two-thirds of the total output of tin-plate is used in the manufacture of tin cans and containers. The greater part of these are used in the preservation of food products, it being estimated that over eight billion cans are used annually for this purpose. Tin-plate of coke quality is used practically universally for this purpose [C 57] except for such products as are very severe in their action on the plate so that perforation of the can during storage becomes a serious problem. Serger's recommendation, based upon German practice [C 51], that the minimum weight of coating on tin-plate used for canning purposes should not be below 0.15 gram per 100 square

centimeters of surface (0.3 gm. per 100 sq. cm. of sheet) agrees well with American practice. This value corresponds to approximately 1.35 pounds of tin per base box.

Much of the trouble which has been experienced in the canning industry in the use of tin cans can be explained by the fact that in no case is the tin coating perfectly continuous. Because of the minute pinholes which are found to an appreciable extent in the tin coating of all grades of tin-plate as made at present there is always contact to some extent between the steel base and the product which fills the container. Much co-operative experimental work has been carried out by the National Canners Association with various manufacturers of material in connection with the production of tin-plate with the hope of obtaining a better commercial product with present-day manufacturing methods [C 29, C 59]. Although the investigations have shown how the qualities of the steel sheet could be improved, particularly with respect to decreasing the tendency toward perforation, it has not yet been found practicable to write specifications for commercial tin-plate for canners' use of any better quality than is now available, with the present manufacturing methods. One important conclusion of the work was that, although an increase in the weight of the tin coating decreases decidedly the tendency of tin-plate to perforation, there is no assurance that such heavy-weight tin-plate is free from pinholes. Tests made by means of the "gelatin test", as shown in Figure 64, indicated the presence of pinholes even in the tin-plate of charcoal grade though not nearly so many as in tin-plate of coke grade.

The opinion was expressed as a result of this investigation [C 59] that the tendency to perforation of tin cans containing canned foods is influenced to a large extent by the quality of the steel as determined by the furnace practice but that the factors which control this appear to bear no relation to the discoloration of cans and contents which is another source of trouble with canners. The discoloration of the inside of cans and of their contents is not influenced to any great extent by variations of the steel base nor by the weight of the tin coating on the plate.

Table 12 from Baker [C 60] summarizes the situation with respect to the use of tin cans in the canning industry.

A great deal of work has been done on the subject of the contamination of canned foodstuffs with tin from the container since Menke [C 1] called attention to this in 1878. According to Bigelow [C 24], recent writers agree that the earlier ideas concerning the toxicity of tin were erroneous. He states that a large part of the tin taken up by canned products from the tin layer of the container is not in solution.

TABLE 12.—RELATIVE VALUE OF TIN CANS IN THE CANNING INDUSTRY [C 60].

Product	Relative Value of the Tin Can as a Container
Vegetables	
Peas	Practically a perfect container.
Tomatoes	No trouble when the article is properly prepared, closed, and cooked.
Tomato pulp and paste	Tin cans are very satisfactory as containers.
Corn	Very considerable difficulty is experienced from discoloration by the formation of iron sulfide by the action of sulfur from the corn on the iron of the steel base. The former freedom from this difficulty, in the days of soldered cans, can be explained by the presence of zinc chloride from the flux used.
Baked beans and red beans	Ideal.
Asparagus	Very satisfactory.
String beans	Eminently satisfactory.
Hominy	Trouble from discoloration; not a defect inherent in the tin.
Sauerkraut	Ideal.
Tomato and other soups	No ground for complaint on any score.
Sweet potatoes	Discoloration, resulting from improper preparation, not attributable to the tin container.
Spinach	Hard product to hold in a tin can, special preparation of the product is necessary, detinning action is rather severe.
Lima beans	Very suitable.
Succotash	Very little trouble experienced.
Okra	A great deal of trouble with discoloration unless special methods are used.
Spaghetti	Eminently satisfactory.
Pumpkin and squash	Severe dissolving action on the tin coating and the contents of the can are affected. An enameled can is highly satisfactory.
Beets	Difficulty in preserving the color; an enameled can must be used.
Fruits	
Pears, peaches and apricots	Almost ideal.
Pineapple	Eminently satisfactory.
Prunes, grapes, raisins, figs	Eminently satisfactory.
Ripe olives	No difficulties experienced.
Rhubarb	Unsatisfactory except for a *short* period of time.
Grape fruit	Special precautions in preparation are necessary, not satisfactory for long periods.
Apples	Trouble from perforations of the cans. Some of this trouble is attributable to method of preparation of the product.
Cherries:	
White	Very little trouble experienced.
Black	"Probably the most severely perforating article ever packed in a tin can."
Red, sour	Much trouble from perforations, some of which is attributable to improper preparation. Charcoal tin plate should be used, an enamel coating is necessary to preserve the color.

TABLE 12.—*Cont'd.*

Product	Relative Value of the Tin Can as a Container
Fruits—*Cont'd.*	
Apple butter	At the best, only a temporary container. Heavy tin coatings should be used.
Jams and preserves	Very little difficulty experienced.
Plums	Same as red cherries.
Berries:	
Strawberries	Not a satisfactory container. The chance of perforation is very high. Enameled cans of charcoal tin plate should be used.
Blueberries	Much the same as strawberries. Enameled cans are not necessary to preserve the color.
Huckleberries	An enameled can must be used to preserve the color, but the chance of perforation is very great.
Cranberries	Should be regarded at best as a semi-perishable article.
Black raspberries	Fairly good results, if not kept too long.
Red raspberries, loganberries	Reasonably safe to can. Enameled cans must be used to preserve the color and charcoal plate will give assurance of added safety.
Canned syrup	Considerable trouble experienced, but on account of improper preparation; the tin plate itself gives no trouble.
Cider	The cans are readily perforated.
Salmon	Excellently adapted for this product.
Oysters	Satisfactory.
Clams	Give trouble on account of discoloration. The tinplate and can not at fault. (See corn.)
Sardines	No trouble attributable to the use of the tin cans.
Tuna fish	Satisfactory, with improved canning methods now in use.
Lobster	Trouble from discoloration caused by iron sulfide.
Shrimp	Satisfactory for the "wet pack," but far from ideal for the "dry pack" on account of discoloration.
Canned meat	Much of the trouble which has been experienced can not be attributed to the tin plate. Heavy grades of tin coating should be used.
Canned milk	Such trouble as has been experienced is not attributable to the tin-plate.

Goss [C 26] also reached the same conclusion. The toxic effect of dissolved tin is now generally considered as being much less than was formerly supposed and the effect of tin which is not in true soluble form as being still less. Zellner [C 69] recently reported upon a series of poisoning cases resulting from food cooked in tinned-iron cooking utensils. The presence of arsenic, 0.04 per cent, in the tin coating was stated to be the cause of the trouble, however.

The belief that many of the cases of accidental poisoning from eating improper foodstuffs could be attributed to the fact that the food had been allowed to remain too long in the tin can after opening it was formerly quite commonly accepted. A few canned products retain

their color better and present a more pleasing appearance if not allowed to remain long in the can exposed to the air. There is no evidence, however, to show that any canned food left in contact with the tin container develops any more toxic properties within a reasonable time than when kept under the same conditions in any other kind of container.

The corrosive attack of tin-plate in the form of tin cans from the contents of the can may be conveniently grouped under three headings [C 88]: (1) discoloration resulting from the formation of iron sulfide by the sulfur compounds in the foodstuffs, for example, corn; (2) a general etching of the tin coating as a small amount of tin is dissolved by the contents of the can; and (3) perforation of the tin plate resulting from a localized corrosive attack on the iron sheet. The latter is by far the most serious type of corrosive attack.

Iron in contact with tin when wet with an electrolyte acts as the anode of the iron-tin couple. Hence, localized corrosion of bare spots on tin plate, resulting from pinhole perforations of the coating after a prolonged attack, might result in the rusting of a hole through the sheet. This is what not infrequently happens in the case of many fruits preserved in tin cans. Mantell and King [C 90] have recently published results which are interpreted as demonstrating a reversal in the polarity of the iron-tin couple when immersed in certain solutions, such as strong electrolytes, and have advanced an explanation on the basis of this phenomenon for the relative freedom from perforation for the majority of canned foods in tin cans. The reversal in polarity is attributed by Mantell to the "ennobling" of the iron by surface film formation, as a result of which the tin acts as the anode of the couple.

Recovery of Tin from Tin-plate Scrap.

On account of the high price of tin combined with the very low price of tin-plate scrap, the recovery of the tin from such scrap has long been a subject of study and investigation. A great number of patents have been granted but only a few of the suggested methods have proved successful in practice on a commercial scale.

The early methods, which were based upon the use of such solvents as ferric chloride and stannic chloride, were too expensive and hence unsuccessful commercially. Likewise the "dry" metallurgical method of partially melting off the tin together with the oxidizing of some of it to the form of "tin ashes" from which the tin was later reduced was not a success. The two commercial methods used with considerable success today are (*a*) electrolysis in an alkaline solution and (*b*) treatment with dry chlorine [C 62].

In the electrolytic method, the tin-plate scrap which after being

cleaned, usually with a hot solution of sodium carbonate, is compressed into bales of suitable size for handling, is made the anode of an electrolytic cell of which the other electrode may be a copper grid or the iron container for the solution. The electrolyte is a solution of sodium hydroxide containing some oxidizing reagent and is kept at approximately 70° C. (160° F.).

Tin is dissolved at the anode to form sodium stannite from which tin is recovered at the cathode in a finely divided condition as a spongy deposit which after removal may be compressed, dried and melted. Experience has shown that a considerable excess of sodium hydroxide as well as the oxidizing reagent over the theoretical amount must be used. The bales of scrap, freed from the tin, are melted and used in the preparation of such products as sash weights. The use for steel making of scrap of this nature which may contain appreciable amounts of tin at times is not favored in American steel practice.

The tin may also be recovered from tin-plate scrap by means of an oxidizing alkaline solvent, such as sodium hydroxide and sodium nitrate, without electrolysis. By keeping the solution at the boiling point for several hours sodium stannate crystallizes from the solution, and can be separated from the liquid by a centrifuge. The stannate is usually converted to the form of tin oxide and is used in this form, principally in the enameling industry.

The chlorine treatment depends on the fact that *dry* chlorine readily reacts with tin at low temperatures but not with iron. The anhydrous stannic chloride which is formed drips off the clean baled scrap and is recovered and used as such. No attempt is made to obtain the tin from this as the tetrachloride finds a ready market, particularly in the silk industry. Although the difficulties attendant upon this process are very great, the process has been developed so that now it is decidedly a commercial success [C 31, C 61].

Electroplated Tin Coatings.

The electrodeposition of tin as ordinarily carried out is used commercially to only a very limited extent for the production of tin coatings. Electroplated tin coatings, as a rule, have a dull appearance and a finishing treatment involving scratch brushing and buffing is necessary in order to obtain a polished surface. The coatings secured by the hot-dipping process are, on the whole, very much more satisfactory. According to Hughes [F 10], the electroplating process is used abroad to a considerable extent to renew the coating on tin-coated articles which are used repeatedly, as in bakeries, confectionery factories and the like. Tin coatings are used on small articles, such as buckles, brackets, lamp

fittings and other ornamental articles as well as on larger pieces like fenders and fire screens for producing an appearance resembling oxidized silver, which may be done by the use of suitable solutions. The contact process, described below, can be used for producing such tin coatings, however, instead of the regular electroplating process.

The solutions used in tin plating must contain the tin in the stannous condition. If the metal exists in the solution as the stannic salt (Sn^{IV}), reduction to the divalent condition must precede deposition. Stannous chloride ($SnCl_2 \cdot 2H_2O$) and sodium stannite (Na_2SnO_2) are the two commonly used salts for solutions [N 21] used for tin plating. On account of the tendency for the electrodeposit to form as "trees", the presence of a suitable colloid "addition agent" is of importance for securing a dense or impervious coating.

The Immersion Process.

Tin may be deposited from solution in the form of a very adherent, although very thin, coating without the application of an external electromotive force such as is necessary in ordinary electroplating. The fundamental principle is, of course, the same in both. In this case, however, the necessary current arises from the contact of the dissimilar metals immersed in the solution. The process has found rather wide application for small articles of brass, iron or steel such as safety pins, thimbles, buckles and many other articles for which a bright finish is desired [C 92].

In one process the brass articles, after cleaning, are piled on wire trays with thin perforated sheets of tin "sandwiched" in at intervals and are immersed for 3 or 4 hours in a hot (90° C., 194° F.) solution of sodium chloride and potassium acid tartrate (cream of tartar, $KHC_4H_4O_6$). The tin forms the anode of the couple and passes slowly into solution and is deposited upon the brass articles (cathode). Immersion in a solution of stannous chloride and sodium hydroxide at the same temperature has also been found to be a satisfactory method for coating brass.

In a slightly different process, scraps of zinc are mixed in with the brass articles which are immersed in a solution of stannous chloride and cream of tartar. The zinc is the anode in this case and as it passes into solution tin is deposited from the solution upon the brass (cathode). The electrolyte, of course, is gradually depleted of its tin. This process is usually carried out in a rotating barrel and a period of 2 to 4 hours at 80° C. (175° F.) is required.

For tinning iron or steel a slight modification of the method has been found necessary. The solution contains ammonium alum in addition

to the other substances named above. The solution is kept hot and a period of about 45 minutes is usually sufficient. In all cases the articles are thoroughly cleaned by rinsing with hot water after the plating solution has been drawn off, after which they are dried and polished somewhat by sawdust, bran, or macerated leather. Although the coatings as deposited are very much brighter than those made by electroplating, coatings made by this method are extremely thin but very uniform. It is not possible to form a heavy coating by this method since the deposition of tin necessarily ceases as soon as the surface is covered. Although the method is an old one and is of some commercial importance, it is still carried on in a strictly empirical manner.

Cementation of Tin.

Guillet [C 98] has investigated cementation by means of tin as a method of obtaining a wear-resistant surface. The method used was essentially the same as used for cementation with other metals except that the temperature was necessarily much lower. Encouraging results were reported for the copper alloys used; with pure copper and nickel, however, only a very slight penetration was obtained.

Tinfoil.

Tinfoil is used extensively as a wrapping, especially for foodstuffs, tobacco, confectionery and similar products. It is made by cold rolling a cast slab of tin down to the required thickness in a series of steps. In much of the "tin" foil made at the present time, however, the tin forms only a layer on each surface, the intermediate portion of the foil being of lead. Such a foil can be readily rolled from a composite ingot made by casting tin around a bar of lead or lead alloy [C 97].

Tinning of Copper.

The tinning of copper is a rather simple matter [C 18]. A good deal of sheet copper is tinned, usually on one side only, and is done by hand. The cleaned sheet is heated from beneath by some suitable means and a small amount of flux (ammonium chloride) and a few scraps of pure tin are dropped on the heated surface. By rubbing with a wad of cotton waste a uniform coating is produced. Much of the sheet copper for roofing was formerly tinned and still is to some extent. Merica [C 25] has described a peculiar type of corrosion of such tinned roofing copper by which perforations of the copper were produced. Exception may be taken, however, to the explanation advanced that the corrosion of the copper was to be attributed entirely to the

electrochemical influence of the copper-tin compound formed in such a coating.

The tinning of copper wire which is to be covered with rubber insulation is a very common practice. The tin layer guards against the corrosive attack of the copper by the sulfur in the rubber and likewise deterioration of the rubber by contact with the copper is prevented to a large extent. The tinning of the copper wire is carried out in essentially the same way as in the zinc coating of wire. Pinholes exist in the tin coating on the copper the same as in the coating on tin plate. These microscopic perforations constitute a means for the gradual ingress of sulfur vapor and a corrosive attack of the copper follows, so that the tin coating is often loosened and strips off from the copper when the insulation is removed. This is often the case with old insulated copper wires.

Chapter 9.

Coatings of Copper, Nickel, Chromium, and Cobalt.

Copper Coatings.

Copper is not recommended ordinarily as a coating for the protection of iron or steel against corrosion. An article completely coated with copper, if the coating were intact at all points, would, of course, resist corrosion as effectively as a piece of solid copper, but only so long as the coating remained intact. The cathodic behavior of copper with respect to iron when the two metals are in contact and wet with an electrolyte is similar to the behavior of nickel in this respect. Copper, however, does not have the pleasing appearance that nickel does and lacks the ability to retain a high polish, both of which are properties that favor the use of nickel as a coating metal in spite of its cathodic nature with respect to iron. As a general rule, copper coatings are used for other purposes than protection from atmospheric corrosion.

Coatings of copper may be deposited very readily by electroplating, by metal spraying and by mechanical coating processes. In addition, some special methods, as noted below, have been proposed.

Electroplated Copper Coatings.

Firmly adherent coatings of copper can readily be deposited electrolytically. The two solutions in common use today which have been used for a good many years, are the acid sulfate and the alkaline cyanide solutions. Copper-plating by means of the acid-sulfate bath is limited somewhat since this solution cannot be used for plating directly upon iron. The "spongy" copper which is deposited on the surface of the iron upon immersion in copper sulfate solution prevents the subsequent deposition of an adherent coat. For coating iron or steel, therefore, the cyanide solution must be used, at least at the start, although it has been stated [D 6], that copper can be plated directly upon iron provided the iron has been covered with a film of arsenic by being dipped into a solution of arsenic trioxide in concentrated hydrochloric acid. The alkaline cyanide plating bath, however, is generally a much more con-

venient means to use in the copper coating of iron and steel than is such a solution of arsenic.

Structure of electroplated copper coatings.—The microstructure of electroplated copper may be described in some detail since it is typical of many features common to electroplated coatings. Considerable study has been done on this subject [D1, D2, D3, D4, D5, D7, D8].

As shown in Figure 45 [D 4], electroplated copper coatings usually consist of columnar or finger-like crystals arranged perpendicularly to the surface of deposition, that is, parallel to the direction of current flow. The grain size and hence the hardness and strength of the deposited coating depend upon several different variables of deposition. Figure 45*c* illustrates the fact that an increase of current density results in a smaller grain size as well as a more irregular structure, a condition usually accompanying higher strength and hardness. Copper deposits made by use of cyanide solutions have a very fine grain size. Likewise addition agents, usually of a colloidal nature, in a plating bath aid in producing a very small grain size. Some of the colloidal matter is carried to the cathode and built up into the structure of the deposit and acts as an obstructant to grain growth in a manner strictly analogous to that in which non-metallic inclusions serve in metals made in the ordinary manner. This is probably not the only reason, however, for the production of small grain size under such conditions.

The structural change which results upon annealing electrodeposited copper, as shown in Figure 46 [D 5], indicates that the copper layer, as deposited, is not in a state of structural equilibrium, but rather in a condition somewhat akin to cold-worked metal. Complete recrystallization of the metal usually results upon annealing. This condition of electrodeposited metals with respect to internal stresses is probably of some significance in accounting for the hardness of such materials [N 24, N 26].

The uniformity in thickness of an electroplated coating depends largely upon the shape of the article plated. As shown in Figure 47 the thickness of a copper coating at the base of a depression, such as a V-groove, may be not more than one-quarter the average thickness of the coat.

Adhesion of electroplated copper coatings.—There has been much speculation concerning the reason for the adherence of an electrodeposit to the underlying or base metal. The surface to be plated, of course, must be *clean* at the start if good adherence is to be obtained. Evans [N 16] states that a deposit will adhere better to a roughened surface than to a smooth one and more firmly to the surface of a soft

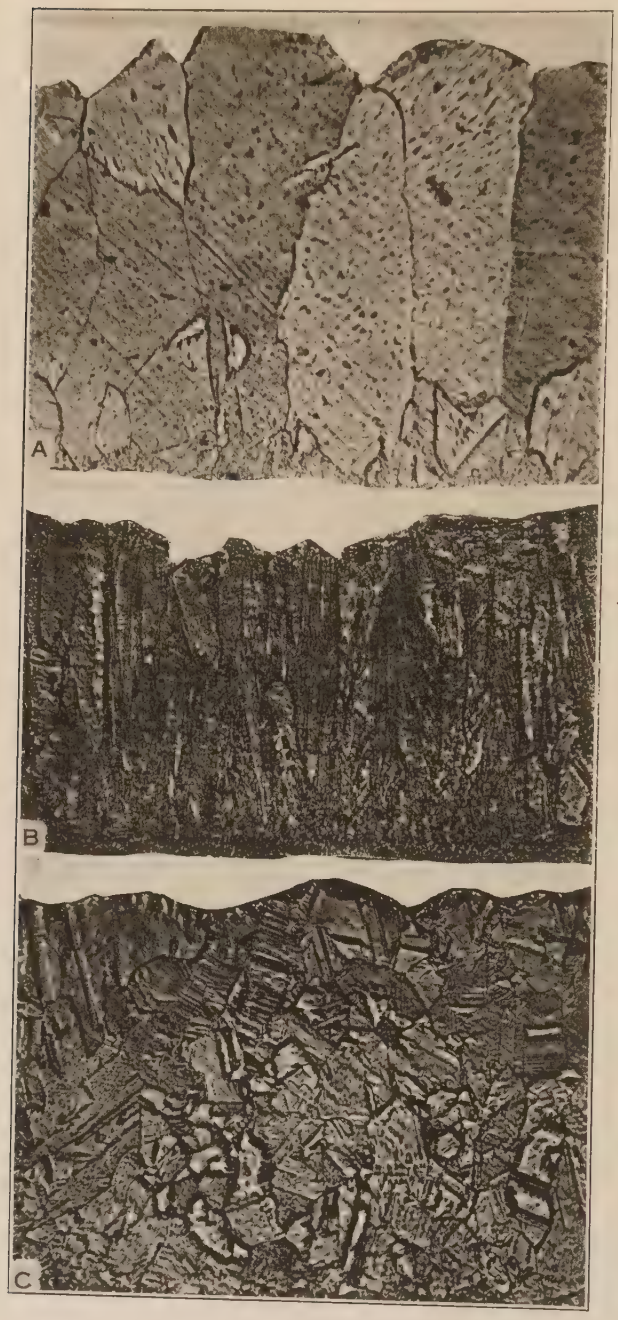

FIG. 45.

FIG. 45. Microstructure of electrolytic copper, × 300. Etchant, ammonium hydroxide containing hydrogen peroxide [D 4].

A, typical coarsely grained deposit; current density 38 amperes per sq. ft. (4.1 amp./dm²); temperature of the bath 40°C; tensile strength of the deposit, 22,000 lb./in².

B, typical columnar structure, current density, 50 amperes per sq. ft. (5.3 amp./dm²), 25°C, tensile strength 41,000 lb/in².

C, irregular structure, current density, 63 amperes per sq. ft. (8.8 amp./dm²), 25°C, tensile strength 42,500 lb./in².

metal than to a hard one. Metals that alloy readily as a rule adhere very well, and there is some evidence indicating an alloying of deposit and base metal at the surface of contact [N 13]. An extreme case of

FIG. 46. Effect of annealing on the structure of electrolytic copper, × 350. [D 5.]

A, The coarsely grained deposit (Fig. 45*A*) did not change when annealed for 2 hours at 600°C, except the layer immediately adjacent to the cathode face which had a fine grain structure, initially.

B, The finely grained deposit (Fig. 45*C*) recrystallized completely when annealed, as in *A*. This shows that the metal as deposited was in a condition of stress.

this is illustrated in Figure 48 which shows the structure of copper electroplated upon a copper base. When the copper specimen which was to be plated upon was etched with acid after the ordinary chemical cleaning, the metal deposited was found to be of such a structure that the crystals in the plated layer were simply extensions of the surface

crystals of the base. After simply cleaning the base metal, however, without etching it, the deposited layer although firmly adherent showed no evidence in its structure of having been influenced by the pre-existing structure of the base metal.

FIG. 47. Variation in coating thickness of electroplated copper depending on the contour of the surface, × 150. [D 4.]

Etchant, ammonium hydroxide, containing hydrogen peroxide.
A, thickness of the layer on a flat surface,
B, layer deposited in a V-groove; conditions of deposition, same as in *A*. Note that the crystals always grow at right angles to the surface of deposition.

The purpose of the acid cleaning was evidently to remove the disturbed and "disorganized" surface layer of metal in much the same way as, in repairing a damaged brick wall, it is first necessary to tear

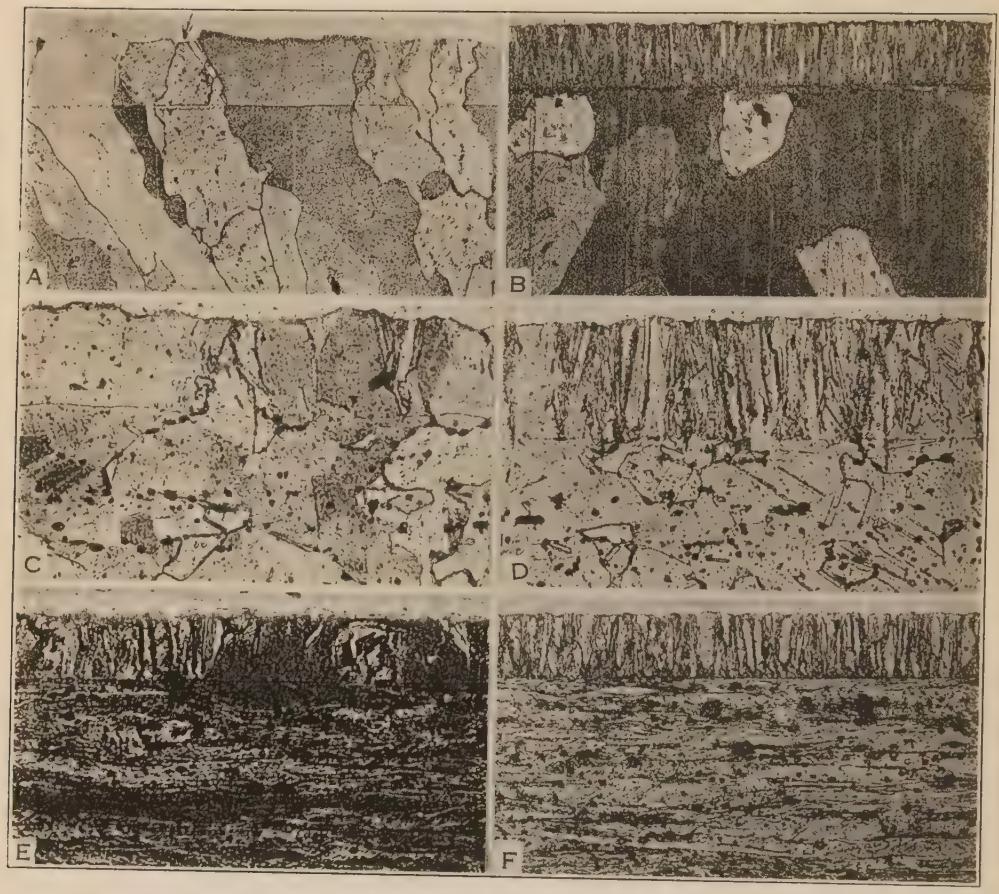

FIG. 48. Effect of the structure of the base metal upon the structure of a layer of copper deposited upon it, × 100. [N 13.]

A, the surface of the base metal, cast copper, was cleaned with nitric acid prior to the deposition of the layer. Note how the crystals of the deposited layer formed as extensions of pre-existing crystals of the base;

B, same as *A*, the base was cleaned chemically but not with acid;

C, same as *A*, with annealed copper sheet as a base;

D, same as *B*, with the base metal of *C*;

E, same as *A*, cold-rolled copper sheet as a base. Note the slight tendency for the structure of the layer to be influenced by the base.

F, same as *B*, with the base metal of *E*.

out all the loosened and broken bricks before the new bricks can be built in as a continuation and extension of the initial structure. Graham [N 18] has recently confirmed the earlier conclusions expressed concerning the structure of copper electrodeposited upon a copper base and made observations on other combinations. It is of interest to note

(Fig. 48*c*) that in the case of copper which had been cold-rolled so that the crystalline structure throughout the sheet was considerably disturbed and broken, the structure of the deposited layer on an acid-cleaned specimen showed only very slight evidence of any tendency to "repeat" the structure of the base.

Fig. 49. Effect of the base metal on the structure of the deposit, × 500. [N 13.]
The crystal indicated by the arrow in the electroplated copper layer of Fig. 48*A* is shown at higher magnification. Note the continuity of crystalline orientation of base metal (below) and electrodeposit (above) as shown by the triangular etching figures.

By means of the x-ray method of examination, evidence of alloying between the base metal and an electrodeposit made thereon can be obtained in cases where direct microscopic examination would show nothing. Frölich and Clark [N 25] have reported, on the basis of such data, that alloying occurs in the electrodeposition of nickel on platinum foil or on nickel. On the other hand, alloying does not occur in the deposition of nickel on aluminum. The ever-present oxide film on the surface of the aluminum prevents the deposited atoms of nickel from

building into the space lattice of the aluminum. There is no evidence in coatings of nickel deposited on aluminum that the growth of the crystals has been influenced or directed in any way.

It is very probable that this feature of alloying of the deposit and the base is one of some importance in determining the adherence of the two, especially if the two metals do not differ widely in their ultimate crystalline structure, that is, atomic arrangement and spacing. It has been observed with other metals, such as silver electroplated on a nickel-silver base [B 118, *discuss.*], and recently the results of x-ray examinations have been interpreted as showing [G 34] that in such a combination of dissimilar metals as lead deposited on platinum the deposited metal had a tendency to adopt the crystal habit of the platinum. This latter statement has not been confirmed as yet.

Use of electroplated copper in selective carburization of steel.—It is often necessary in the case-hardening of steel parts that portions be left in their initial or relatively soft condition so as to allow machining to be done in such parts or to enable the piece to be straightened after hardening. Copper coatings play an important part in this process. Those portions of the surface which are to remain soft are electroplated with copper before the steel parts are packed in the carburizing mixture. At the close of the carburizing treatment, it is found that the presence of the copper layer has prevented carburization of the underlying steel and hence such parts do not harden appreciably when the piece is heated and quenched for hardening.

Copper applied by the metal-spraying process has been found to be effective in protecting against carburization [D 20]. Such a layer must be somewhat thicker than one which is electroplated, since the metal-sprayed layer may be slightly porous. The process is to be recommended because of the ease with which it can be used in applying a copper layer on a few spots, here and there, on an article to be carburized. It is a very simple matter to localize the deposit. Other conditions have favored the use of electroplating, however, and the metal-spraying process has not, as yet, found application in commercial carburizing plants in this country.

It is generally agreed that any coating that will prevent the access of the carburizing gas (carbon monoxide) to the underlying steel will answer the purpose [D 27]. Copper is the most useful of the metals, however. Guillet [D 20] has shown that nickel coatings are not suitable for the purpose as the carbon monoxide readily permeates it and carburizes the steel beneath. Cobalt would be expected to behave similarly and the melting points of the other coating metals commercially available are so much lower than the temperature used in car-

burizing as to be of no value. In practice, various kinds of non-metallic cements and pastes, sometimes containing powdered metals, are used [D 25, D 26]. They are not so dependable, however, as copper plating.

A layer 0.005 inch thick is generally considered as sufficient for ordinary purposes. Lothrop [D 19] recommended this as a minimum thickness several years ago and the results shown in Table 13 by Vanick and Herschman [D 26] support this recommendation. Maeder [N 21, p. 186] has described a very simple test, consisting in the application of a drop of 1-1 nitric acid to the copper surface, to show the approximate thickness of the layer. The time required for the acid to

TABLE 13.—EFFECT OF VARIATION IN THE THICKNESS OF COPPER LAYER IN THE SELECTIVE CARBURIZATION OF IRON [1] [D 26].

Set	Thickness of Copper Layer		Carburizing Period	Depth of Carbon Penetration
	Inch	Mm.	Hours	Mm.
1	0.00025	0.006	12	0.775
			24	2.36
			36	1.81
			48	3.58
			60	4.90
			72	7.31
2	0.0005	0.013	12	0.0
			24	0.86
			36	0.0
			48	2.10
			60	2.33
			72	2.72
3	0.001	0.025	12	0.0
			24	0.0
			36	0.0
			48	1.94
			60	0.94
			72	4.42
4	0.0015	0.038	12	0.0
			24	0.0
			36	0.0
			48	0.0
			60	0.0
			72	2.33
5	0.002	0.05	12, 24, 36, 48, 60 and 72	0.0
6	0.003	0.076	12, 24, 36, 48, 60 and 72	0.0

[1] Open hearth iron was carburized in a mixture of 40% charcoal, 40% barium carbonate, and 20% dry bone at 925° C. (1700° F.).

eat through the copper to the iron base is noted. For a coating 0.0005 inch thick the time required is about 45 or 50 seconds.

Mechanical Copper-coating Process.

The coating of steel with copper by use of the molten metal has been the subject of active investigation since the early part of the last century [D 14]. The difficulties attendant upon the high temperature

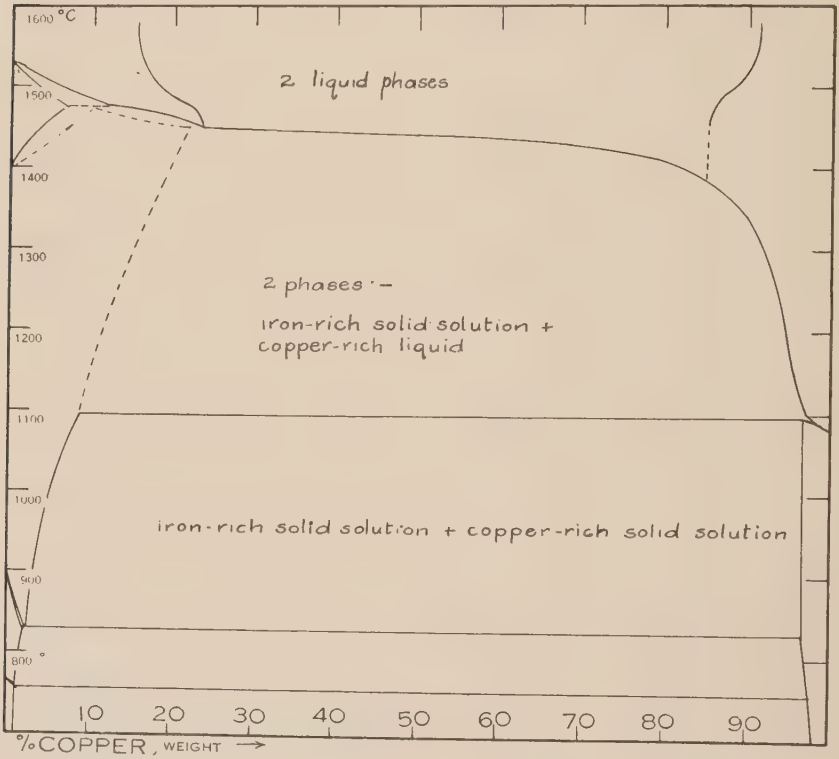

Fig. 50. Equilibrium diagram of the copper-iron alloy system [D 15].

necessary in using molten copper have precluded the use of the simple hot-dipping process.

The equilibrium diagram of the copper-iron system as determined by Ruer and Goerens [D 15] is given in Figure 50. The two metals alloy quite readily although they are not completely miscible in the molten state. Copper, at a temperature just below its melting point (1083° C., 1981.4° F.), can hold in solid solution approximately 3 per cent of iron. At the same temperature, iron dissolves approximately

8 per cent of copper. In both cases, the limit of solid solubility of one metal in the other decreases, as the temperature is lowered, to considerably less than one per cent at room temperature. Most alloys of the two metals therefore will consist of two constituents which are the two solid solutions, the relative amount of each constituent depending upon the composition.

In brief, the mechanical method which has been developed for coating steel with copper is to prepare a composite or duplex billet or ingot having a steel center and a copper casing, which is then rolled or drawn down to the desired shape. No unusual difficulties have been experienced in the rolling of such a composite billet, and the copper coating which results is much more impervious than an electrodeposited one of the same thickness.

Different methods have been proposed for the preparation of the duplex billet. According to the method described by Tassin [D 12, D 13] for "copper clad" steel, the properly cleaned steel billet was heated red-hot and then momentarily immersed in a hot bath of molten copper so as to form a very thin uniform alloy layer over the entire surface, after which molten copper at a much lower temperature was cast around the billet. The casting was accomplished by means of a special mold which, with the billet inside, was totally immersed in the bath of molten copper.

In order to minimize the formation of an alloy layer between the two metals, the "copper-weld" process was developed. This, according to Handy [D 14], consisted in the electroplating of the cylindrical steel billet with copper and then enclosing it in a neatly fitting cast-copper tube. After luting the crevices at the end to prevent access of air, the billet was heated to approximately 950° C. (1740° F.) and then worked into the desired shape. A somewhat similar and earlier process [D 11] consisted in dipping the steel billet in molten copper so as to form a thin layer over the surface and then adjusting the copper sleeve and working it into shape as just described.

The method of casting copper directly around a hot steel billet enclosed in a suitable mold [D 16] is the simplest and is used commercially today. The composite billet can readily be worked mechanically at a temperature of 900° C. (1650° F.). The properties of the finished coated product do not appear to be adversely affected by any increased alloying of the copper and iron which may result from this method. Brass and cupronickel may also be used for coating steel by this method.

Most of the steel coated with copper in this way is made into wire. The combination of high electrical conductivity and high tensile properties make this material a very useful one. The amount of copper

used is dependent upon the desired conductivity of the finished wire. Such wire is usually designated in terms of the conductivity of a copper wire of the same size, for example, "30 per cent conductivity."

Some use has also been made of the copper-coated wire in screen cloth. Some copper-coated sheets rolled from a composite bloom have been made and used to a very limited extent for spouting, eaves-troughs and the like. Its use for bullet jackets has given very encouraging results. During the war, instead of the usual cupronickel bullet jacket, the Germans developed one made from a soft steel sheet coated with cupronickel by a process similar to that described above.

Miscellaneous Copper-coating Methods.

Richards [D 18] has described a method for coating steel with copper in which the copper is reduced from the oxide and melted *in situ*, that is, on the surface to be coated. The reduction of copper oxide by reducing gases such as carbon monoxide or hydrogen begins at a relatively low temperature, for example, as low as 130° C. [D 18*a*]. A mixture of powdered copper and copper oxide in crude oil ground to a consistency of a light varnish was applied by Richards to sheet steel while cold by means of rolls much like the inking rolls on a printing press, and the coated sheets were then conveyed by a chain conveyer into a furnace maintained at a temperature well above the melting point of copper. It was claimed that the oil base reduced the copper oxide present and also prevented the oxidation of the copper which melted on the surface of the sheet. Although the method has been tried out on a commercial scale, and apparently with pronounced success, such sheets are not regular commercial materials.

The process is an adaptation of the earlier Siemens process used for the "coppering" of carbon brushes for electric generators and motors. In the Siemens process, the copper film is formed on the surface of the carbon by packing the brushes in fine divided copper mill scale (oxide) and heating to a temperature of approximately 400° C. The reduction of the oxide to metallic form gives a very adherent thin film of copper on the surface of the carbon. A process carried out in a manner quite similar to the Richards process is also utilized in ceramic work.

A method often employed for producing a copper finish on wire consists in the immersion of the wire in a solution of copper sulfate. The precipitated spongy copper is rendered firmly adherent by drawing the wire through a die and reducing it in size very slightly. The coating thus formed is primarily for improving the appearance of the wire rather than for protecting it from corrosion.

Brass Coatings.

The simultaneous electrodeposition of copper and zinc so as to form a coating of brass can be accomplished quite readily by the use of a cyanide solution of the two metals. In ordinary solutions, for example, sulfates, the difference of potential between copper and its solution (copper ions) varies so greatly from that between zinc and its solution (zinc ions), that the simultaneous deposition of the two metals is impossible. In a cyanide solution of the proper concentration, however, the potentials of the two metals are so nearly the same that copper ions and zinc ions can be discharged at the same time on the cathode and a layer of brass be formed. Examination by means of the x-ray diffraction method of the deposit formed has shown that such a deposit is a true alloy of the two metals and not merely a mechanical mixture of small crystals of copper and zinc.

Brass coatings are used quite extensively on iron and steel articles, especially upon builders' hardware, to give the appearance of solid brass. Such coatings are primarily for appearance. As a rule they are very thin and afford little protection from atmospheric corrosive agencies. Brass-plated iron and steel articles rust very readily when used for out-of-door exposure. The protection afforded by such coatings against atmospheric corrosion would be increased by using a preliminary layer of zinc. It is doubtful, however, whether this practice would prove entirely satisfactory. According to Traub [B 189] an electrodeposit such as gold or copper on top of a zinc deposit gradually fades in color as a result of the gradual diffusion of the outer metal into the underlying zinc layer.

Nickel Coatings.

Nickel coatings are used very extensively. Electroplating is the method employed, practically exclusively, for producing such coatings, which are applied to the finished articles and not to sheet and wire, as a rule. The first record of nickel plating was in 1843 and nickel plating as an industry dates from 1870. In the use of nickel coatings, the decorative idea outweighs that of simple protection. Nickel has a very pleasing appearance when polished and since it is quite resistant to atmospheric corrosion only a little attention is needed in order to maintain the high luster of the polished surface.

Nickel coatings are used largely on copper alloys, especially brass, and on iron and steel. They afford no protection other than in a mechanical way by excluding air and moisture and, in the case of nickel-plated iron or steel, perforations in the coating are soon made manifest by the appearance of iron rust at those points. The results obtained

by Thomas and Blum [E 31, E 37] in a recent study of the protective value of nickel coating have served to emphasize strongly the need of obtaining impervious coatings largely by increasing the thickness of the coating in order to assure protection of a steel base from corrosion.

The average thickness of commercial nickel plating is rarely over 0.0003 inch (0.0076 mm.) and is frequently less than 0.0001 inch [E 29]. An increase in the average thickness of commercial nickel coatings is very desirable. A minimum thickness of 0.001 inch (0.025 mm) has been recommended [E 5, E 31] in order to ensure a reasonably high protective value for such coatings.

Nickel is deposited from a nearly neutral or slightly acid solution in which the nickel is present principally as a simple salt, usually the sulfate. It can be plated directly upon steel but often a preliminary coating of copper is used, and frequently the coating is deposited in three layers: nickel, copper, nickel. This practice is recommended for obtaining superior corrosion resistance with nickel coatings especially on parts such as bumper bars and other motor car fittings, as well as other articles which are subjected to severe weather conditions. The following results by Baker [E 28] show that when subjected to accelerated corrosion the resistance of a nickel coating deposited as a single layer is decidedly less than the resistance of a coating containing the same amount of nickel in the form of two layers with a film of copper sandwiched between.

TABLE 14.—RELATIVE RATING OF NICKEL COATINGS ON THE BASIS OF ACCELERATED CORROSION TEST[1] [E 28].

Specimen	Coating Thickness, Inches				Rating of Coating
	Nickel	Copper	Nickel	Total	
1	0.00036	.....	.....	0.00036	5.0
2	.00009	0.00027	0.00018	.00054	19.5
3	.00018	.00027	.00036	.00081	59.0

[1] Sodium chloride spray test (p. 226) was used.

Exposure tests of sheet steel nickel plated in various ways, the thickness of coating being the same in all cases [E 37] have likewise shown that the corrosion-resistance of such coatings in the weather is noticeably superior to that of nickel coatings deposited as a single layer. These exposure tests have failed to show any decided superiority in the corrosion resistance of pure nickel coatings over that of commercial nickel coatings or of those containing as much as one per cent of iron, which is a common impurity in commercial nickel anodes used for electroplating purposes. It has been shown by Thompson [E 22] that

FIG. 51. Microstructure of nickel coatings, × 100.

A, section of an electroplated coating deposited from a sulfate bath containing additions of fluorides [N 15]. This coating is much thicker than the average nickel plating.

B, iron coated with nickel on both sides by the mechanical process [E 29]. The coating comprised about 5 per cent of the thickness of the coated sheet.

C, material similar to *B*, except that the coating comprised 20 per cent of the thickness of the coated sheet.

nickel coatings containing a slight amount of iron are whiter, denser and more finely grained than those of pure nickel. Inclusion in the deposited layer of particles of a colloidal basic iron precipitate may, however, give rise to some porosity in such coatings. The hardness of the electrodeposited nickel varies within rather wide limits according to the

conditions of deposition. McNaughton [N 24] has reported the Brinell hardness number as ranging from 180 to 420; the latter value approaches the hardness of a quenched-and-tempered high-carbon steel. The Brinell hardness number of an annealed nickel sheet is approximately 80 to 100.

A preliminary layer of zinc or of cadmium is sometimes used in nickel plating. Such coatings would be expected to protect iron better than a simple nickel layer would. As a rule, however, such coatings, especially those of nickel on zinc, do not retain their bright metallic luster when exposed to corrosive conditions so well as coatings in which zinc is not used [N 21].

In microstructure, an electrodeposited nickel coating is quite similar to other electroplated coatings although the grain size is usually much smaller. This is shown in Figure 51.

A factor of importance in determining the adherence of a nickel coating to its base is the fact that such coatings are frequently highly stressed internally in tension, as deposited, so that the coating may strip off in close tight rolls after a break has been started. It was shown over 50 years ago [N 1] that films of metal produced by electrodeposition are often in a highly stressed state. The simple experiment of depositing metal on the outside of a thermometer bulb showed this very conclusively. Much investigation of this phenomenon has been carried out [E 6, E 12, E 17, E 21]. Stoney [N 2] demonstrated the existence of a tensile stress as high as 43,000 pounds per square inch in a nickel coating which, by being deposited on one side of a steel ruler, caused the ruler to bend into a bow, the coating being on the concave side. Complete agreement as to the cause has not yet been reached. However, it appears to be related to the inclusion in the nickel of the hydrogen simultaneously deposited with the metal although many of the German investigators are inclined to attribute this behavior of electrodeposited nickel films to the presence of iron. Thompson [E 22] concluded that in all probability both of the factors are involved. Coatings which are very highly stressed are usually detected before they are put into service. Such coatings are more prone to failure under corrosive conditions than similar ones not so stressed. Any corrosion occurring between coating and base originating because of pores or pinholes in the coating may serve as a start for the peeling of the coat.

Special Applications of Nickel Plating.

A good deal of attention has been given to the nickel plating of aluminum and aluminum alloys [E 8, E 9, E 18]. Most of the methods

which have given any satisfaction have depended upon the fact that during the cleaning of the surface, which must be very thoroughly done, the surface was roughened considerably. The degree of adherence of the coating evidently depends in large measure upon this roughening of the surface. The peeling of a nickel coating from the aluminum base when the article is exposed to severe or prolonged atmospheric corrosion is not at all uncommon, however. A recent application of the nickel plating of aluminum or light aluminum alloy is in the manufacture of articles of sheet aluminum alloy such as gasoline tanks for airplanes, which must be soldered. The nickel can be readily and successfully soldered, whereas the soldering of aluminum cannot be relied upon as being stable in the presence of moisture.

It has been shown [E 11] that by nickel plating brass articles which are subject to deterioration by season cracking resulting from the combined action of internal tensile stress and a surface corrosive attack, such deterioration can be prevented.

Nickel coatings are also applied to zinc and zinc-base alloys such as are used for die castings. Such coatings often peel off under severe atmospheric corrosion in the same manner as nickel plated on aluminum. Such coatings should serve a very useful purpose, however, when they are successfully applied, in eliminating, or at least retarding, the hardening and warping change which a die-casting may undergo, largely as a result of a slow corrosive attack.

Nickel coatings because of their superior wear-resisting properties are used to a considerable extent on copper electrotypes and to a smaller extent on stereotyped plates. They serve as protective coatings, not only in a mechanical sense by resisting wear but also in a chemical way, since they withstand the chemical action of colored ink much better than copper does [E 29].

An interesting case of the application of nickel plating to a semi-finished product is exemplified in the manufacture of the plates for the Edison storage battery [E 29a]. A long thin strip of cold-rolled steel is coated by passing it in proper sequence through the necessary cleaning baths, plating solution and washing tanks, from which portions are cut off and fabricated into the tubular and flat containers used for the flake nickel and other substances required in the preparation of the assembled battery plates. In order to obtain good adherence of the nickel coating to the base, the strip is annealed in a hydrogen atmosphere before being cut up and formed into the shape of the containers.

"Nickel-clad" Steel.

Nickel-coated sheet steel has been made by hot-rolling a composite billet (steel core and nickel exterior) by a process similar to that described for copper. On account of the high melting point of nickel (1452° C., 2646° F.), electrodeposition has been used to build up the nickel casing of the composite billet rather than pouring molten nickel around the steel.

The same object can also be accomplished in a somewhat different manner [E 38, E 29]. A sheet-bar of steel, after cleaning, is placed between two thinner plates of nickel and the whole is enclosed in a protective wrapping of thin sheet steel. After being heated in a reducing atmosphere to a suitable temperature, the composite sheet-bar is rolled to form a solid composite sheet. The outer steel layer resulting from the protective wrapping of steel sheet can be removed by pickling. Figure 51 shows the microstructure of an open-hearth iron sheet coated with nickel by this method.

The market for such material as yet is very limited and the material does not rank as a regular commercial product. The coating on nickel-clad steel is very decidedly thicker than the average electroplated nickel coating and much superior to it in being free from pinhole perforations.

Chromium Coatings.

Chromium Cementation—"Chromizing".

A coating of chromium on iron may be produced by a method analogous to that used for sherardizing and for calorizing. In the method described by Kelly [F 3], the parts to be treated are packed in a container with a mixture of 55 parts chromium powder and 45 parts alumina by weight and heated in vacuo or an inert atmosphere, preferably of hydrogen. It is important that there be no traces of oxygen or water vapor present in the gas since at the high temperature necessary for this process (1300-1400° C., 2370-2560° F.) the chromium would quickly be rendered inactive by formation of a film of oxide. The chromium powder used should be of 95 per cent purity at least; the alumina is used merely as a diluting agent. Laissus [F 6] has recently investigated the chromizing process and confirmed most of the conclusions of the earlier work of Kelly. He found, however, that he was able to obtain very good coatings by means of powdered ferrochromium and that if care was used in luting the openings around the covers of his containers it was not necessary to use a hydrogen atmosphere.

The metals, chromium and iron, alloy very readily with one another. Different investigators of this system have reached rather widely varying conclusions concerning the equilibrium diagram of this alloy system. Janecke [F 1] reported that iron and chromium form a simple eutectiferrous series of alloys, the eutectic temperature being approximately 1315° C. with the eutectic containing 75 per cent chromium. Each of the metals was reported as being soluble to a very considerable extent in the other. Murakami [F 2] concluded, however, that the alloys of the iron-chromium binary system form an unbroken series of solid solutions. Pakulla [F 5] recently reached the same conclusion as the result of an independent investigation. The fact that chromium readily enters into solid solution in iron is a very favorable condition for the chromizing process.

The chromizing coating process can readily be used with iron or low-carbon steel. With high-carbon steel, however, Kelly [F 3] reported difficulty and found it necessary to decarburize the surface before applying the chromizing treatment. The behavior of a chromized metal when heated is similar to that of a calorized material. The chromium diffuses deeper into the metal as the heating is continued and the chromium content of the surface layer is gradually reduced. The chromium content of the surface layer on an iron sample which was treated for three hours at 1350° C. was reported by Kelly to be 10.4 per cent. By heating a similarly treated rod for three hours more in hydrogen the chromium content of the surface layer was reduced to 7 per cent.

The microstructure of a chromized iron sample is shown in Figure 52. The chromium is evidently in solid solution in the iron.

The surface of a chromized metal is not hard and can readily be polished. Kelly reported that when exposed in the salt-spray box (p. 226), chromized iron resisted corrosion as well as sherardized specimens and after a month's exposure showed only here and there a slight evidence of corrosive attack. Specimens chromium coated by this method were found to have a decided resistance to attack by dilute nitric acid, but were very readily attacked by dilute hydrochloric and sulfuric acids. He also concluded that chromized nickel steel will withstand erosion exceptionally well when used as turbine buckets.

On account of the marked advances which have been made in the production of coatings of pure chromium by electrodeposition, the chromizing process has not been used to the extent that it might otherwise have been.

Various processes for producing a surface layer of chromium on steel or iron castings have been developed and patented [F 22]. Essen-

tially, these processes consist in covering the face of the mold in which the casting is to be made with powdered ferrochromium made into a paste with a suitable binder, for example, sodium silicate. When the molten metal is poured into the mold, it alloys to a considerable extent

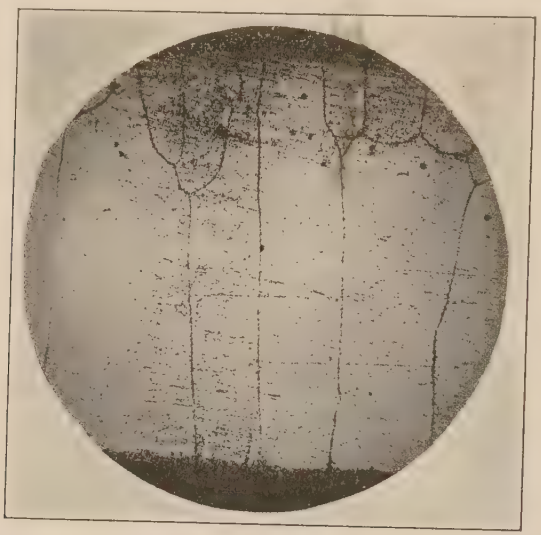

FIG. 52. Structure of a coating produced on iron by "chromizing," heated for 4 hours at 1350°C, × 50. [F 3.] The upper edge corresponds to the outer surface of the coated material.

with the chromium facing. As yet such processes have not been used commercially, however, to any extent.

ELECTROPLATED CHROMIUM COATINGS.

Metallic chromium was obtained by electrolysis of an aqueous solution by Bunsen as early as 1854. It was only very recently, however, that electroplating by means of chromium became successful enough as to be considered as having commercial possibilities. A solution of chromic anhydride (CrO_3) with a small amount of chromium sulfate is generally used for the purpose, together with insoluble anodes, such as lead [F 8]. A very careful control of the conditions of electrodeposition is necessary, however [F 13, F 20, F 23]. The metal can be deposited in an adherent coating upon iron, steel, copper, brass, nickel and cobalt, but as yet satisfactory adherent coatings have not been produced on zinc, aluminum, or cadmium, according to Ollard [F 19].

The value and many of the applications of chromium coatings depend upon the great hardness of the metal together with its ability to take a very high polish and retain it even under severe corrosive condi-

tions. Electrodeposits with either a matt or frosty surface or with a bright or polished surface, the excellence of which is essentially equal to that of the base upon which it is deposited, can be obtained according to the plating conditions used. According to Haring [F 20] the gray or matt condition is a "burnt" deposit. The existence of two allotropic forms of electrodeposited chromium as reported by Ollard [F 23] has not been verified by other investigators. The bright deposit is the one to be obtained if possible, although the matt surface will take a satisfactory polish if proper polishing methods are used [F 23].

A chromium coating affords only mechanical protection from corrosion and in order to obtain good protection an impervious coating is required. Like electroplated nickel, chromium coatings are, as a rule, somewhat porous. Ollard [F 19] has reported that chromium-plated steel rusted quite readily when exposed in a rather severe industrial atmosphere, the chromium layer though unattacked became detached by the rusting of the iron under it. Others [F 14, F 19, *discuss.*], however, have reported that a chromium coating will protect steel against corrosion indefinitely. Chromium readily assumes a passive condition, and it is therefore likely that it neither accelerates nor retards, in an electrochemical way, the corrosive attack of iron in close contact with it. The physical character of an electroplated chromium coating can be very appreciably improved by depositing a preliminary layer of another metal, preferably nickel, which should be buffed before the chromium is deposited upon it. The protection afforded by such a coating against corrosion is very decidedly better than that of a single layer of chromium, unless the latter is made quite thick. The same attractive appearance is obtained by using a very thin "finish" of chromium on top of a nickel or a nickel-copper coating as by using a relatively thick chromium coating. Most commercial applications of chromium plating in which appearance is the important factor, for example, plumbing fixtures, motor car parts, and similar articles, are made in this way.

One of the most important applications of chromium plating is its use as a protection against wear or abrasion. Chromium deposited in the bright condition is "file hard", the matt deposits are not quite so hard. Reliable figures as to the hardness of electrodeposited chromium, by the usual methods of hardness measurements, are not available.

The face of the plates used in printing can be made to have a very much longer life if they are plated with a thin layer of chromium [F 20]. This feature is of decided value when a long life is important either because of the high initial cost of preparation of the plates, as in the case of the plates for printing paper currency and the like, or

because of the very large number of impressions that are to be made. The high degree of polish of the chromium surface as deposited, when properly done, makes it possible to coat the finished plate with a thin layer of chromium without sacrificing any detail of the engraved design. The hardness of the chromium face insures a long life.

Some very promising results have been obtained at the United States Bureau of Standards [F 24] with chromium-plated plug gages. Such gages, though made of a soft steel, have proved in laboratory tests very much superior to similar gages in which the necessary surface hardness had been obtained by heat treatment of the steel. When used in metal-on-metal wear tests, that is, with no abrasive, 200,000 gagings were made with the chromium-plated gages before the diameter of the gage was reduced by 0.001 inch. The wear-resistance of the nearest competing hardened-steel gage was only one-fifth that of the plated ones. In other wear tests, in which a small amount of abrasive powder was introduced between the two metal surfaces, the chromium-plated gages also proved better than the other types, although in this case the difference in wear-resistance was not nearly so pronounced as before. The resistance of the chromium-plated gages was approximately 30 per cent higher than that of the best of the hardened-steel gages. The high hardness and wear-resistance of a chromium coating have encouraged its use also on such moving parts as cams, pins and the like. On account of the very low throwing power of chromium solutions in the deposition of the metal, this method is applicable only to relatively simple shapes, however.

The high reflecting power of chromium has led to the use of chromium plating for reflectors for automobile head lights and other similar reflectors [F 21]. Although the reflecting power of polished chromium is considerably less than that of polished silver (70% for $\lambda = 0.579\mu$ as compared with 93% for silver under same conditions, Smithsonian Tables) which is the metal used at present for the finish on most reflectors, the ability of chromium to remain untarnished has encouraged its use for this purpose. Such reflectors resist abrasion remarkably well on account of the hardness of the chromium.

For articles which must be used at elevated temperatures, such as flat irons, chromium plating is noticeably superior to other coatings, such as nickel. The successful use of chromium-plated rolls used in the glass industry and molds for glass bottles are important examples of the use of the coating for elevated temperatures service. Very encouraging results have also been obtained in the chromium plating of the dies used in making die castings [F 23 *and discuss.*] as well as dies for drawing rods and tubes. Not only is the life of such dies mate-

rially lengthened but also the hardness of the chromium surface insures freedom from scratches on the dies and hence a very smooth surface on the material drawn through such dies.

The excellent resistance offered by chromium to corrosive attack by sulfur and sulfur compounds suggests the use of chromium plating for apparatus in which corrosion of this type is of paramount importance, as in oil-cracking [F 27]. Although many such applications are as yet only in the experimental states the results are very encouraging. Chromium plating of springs, diaphragms and other parts of devices used for the automatic control of the flow of illuminating gas should be of decided value in increasing the useful life of such apparatus. Failure of such devices usually occurs as a result of corrosion by hydrogen sulfide of the springs or diaphragm which are usually made of a copper alloy. The chromium plating of the metal parts used in the vulcanizing of rubber has already proved a decided success. In fact, chromium plating promises to be one of the most successful means of protecting metals against corrosive attack by sulfur, sulfides, and other sulfur compounds.

Attempts have been made to improve the ductility of a chromium coating by alloying with some other metal, such as nickel, for example, by depositing alternate layers of nickel and chromium and then heating the coated article to a high temperature so as to permit alloying of the two metals with each other and with the iron base. Any improvement in the ductility of the coating by such a means is obtained only by sacrificing to a large extent the characteristic properties of a chromium coating, that is, its great hardness and ability to take and retain a high polish.

Cobalt Coatings.

Coatings of cobalt can readily be obtained by electroplating. The coating is very white with a bluish cast and can be deposited on all of the common metals. The hardness of electrodeposited cobalt varies somewhat according to the conditions of deposition but not so widely as nickel. McNaughton [N 24] has reported the Brinell hardness number to range between 270 and 311. Kalmus and his associates [E 40] have made extensive studies of cobalt plating both under laboratory and commercial conditions and have reported very favorably on its commercial possibilities. At the present time, however, cobalt plating is not being used enough to justify classifying it among commercial coating processes.

Chapter 10.

Coatings of Lead, Cadmium, and Aluminum.

These three coating metals are classed together principally because of the similarity in their physical properties, all of them being soft and having a relatively low melting point. There are pronounced differences in their properties as coating metals for iron and steel, lead being electropositive toward iron, whereas cadmium and aluminum are electronegative and hence resemble zinc in their behavior.

Lead Coatings.

Lead has many desirable features as a coating metal. Lead-coated sheet may be very seriously deformed without having the coating stripped off, hence such material finds considerable application in deep-stamping operations in which the coating aids materially by acting as a lubricant. The paint-holding properties of lead coatings are excellent. Lead is the only common coating metal which is resistant to sulfuric and sulfurous acid fumes.

Coatings of lead or lead-rich alloys are deposited by the hot-dipping process, by electroplating, and by the metal-spray process.

The Hot-dipping Process.

When an iron or steel article is immersed in a bath of molten lead, no alloying occurs between the two metals even though the surface may have been thoroughly cleaned previously to immersion. The molten lead, therefore, does not readily "wet" the surface as zinc and tin do, and instead of forming a thin surface film over the immersed article, the lead coalesces more or less into drops and rivulets when the article is withdrawn from the lead bath. The same is true for brass and copper articles immersed in molten lead. Although lead coatings can be produced on iron and steel if great care is taken in cleaning the surface before attempting the hot-dipping process, such coated articles are always more or less unsatisfactory on account of the pronounced discontinuities in the coating that exist. The claim has been made [G 18, G 20] that if clean steel is dipped in a fluxing bath consisting of a saturated solution of zinc chloride containing 5 per cent ammonium chloride immediately before immersion in the molten lead (at 340° to

360° C.), a quite uniform coating of lead can be produced. Usually it is necessary to give the article two dips both in the flux and the lead bath.

In order to form a "bond" for a lead coating, it is necessary to make use of some alloying element common to the two metals, lead and iron. Tin has been used for this purpose for many years as it alloys readily with both metals. Antimony may be used [G 9] and the use of cadmium [G 6] and of mercury [G 3, G 8] have also been attempted with some success. Arsenic has also been recommended [G 18].

The alloying element may either be added in a considerable amount to the lead bath as is the case in the manufacture of terne-plate as described below, or a film of the alloying element may be precipitated on the surface of the article which is to be coated, by immersion in a suitable solution prior to passing through the molten metal bath. Electroplating with a suitable bonding metal before dipping so as to form the desired bonding film has also been used to a limited extent.

Lead coatings show a rather pronounced tendency toward the formation of pinhole perforations as the coating solidifies. In the case of sheets such perforations can be removed by rolling the sheet after it has been coated. On articles of irregular shape, however, this cannot be done.

Baskerville [G 9] has described a process for the production of coatings of relatively pure lead on iron and steel. The material, after pickling, is immersed in a solution of antimony chloride; the film of precipitated antimony serves, by its alloying action after immersion in the bath of molten metal, as a binder for the coating. The molten metal bath used may be either commercially pure lead or an alloy of lead and antimony.

Antimony alloys very readily with lead. The two form a simple eutectiferrous series, the eutectic containing 13 per cent antimony and melting at 274° C. The limit of solubility of antimony in solid lead has recently been shown [G 22] to be as low as 0.5 per cent at room temperatures, increasing to 2.45 per cent at the eutectic temperature. Antimony also alloys readily with iron in a manner very analogous to that of tin and iron. Two compounds, Fe_3Sb_2 and $FeSb_2$, have been reported in this alloy system [G 2].

A somewhat similar process, in which the articles to be coated were passed through a solution of mercuric chloride, has been tried out on a commercial scale. The film of precipitated mercury served as the basis of the alloy-binding layer. On account of the dangers attending the use of the poisonous mercury solution, however, the process did not prove a commercial success [G 3, G 8].

Some excellent "lead-coated" sheets have been made by using galvanized stock as a base upon which the lead coating was formed by immersion in molten lead. Commercial tin plate can be used in the same way as a base for subsequently coating with lead.

Much secrecy is usually observed with respect to lead-coating processes. The principles involved, however, are those outlined above and the chemical analysis of coatings ordinarily described as "pure lead" invariably shows the presence of some other metal which was used as the alloying or bonding agent. One such coating described as pure lead had the following composition: lead, 95.8 per cent; tin, 3.8 per cent; and antimony, 0.4 per cent. A coating of approximately this composition might have resulted had the metal been dipped in an antimony solution, as indicated above, prior to immersion in the bath of molten lead, to which an appreciable amount of tin had been added.

Terne-plate.

This material, commercially often known as "roofing tin", is not infrequently confused with true tin coatings. The name, "terne", meaning dull, was originally used in contradistinction to "bright tin", that is, tin-plate. The composition of terne coatings varies within rather wide limits. Commercial terne coatings with a tin content as low as 12 per cent are made as well as some containing as much as 50 per cent. The most commonly used one in this country, however, is that of 75 per cent lead and 25 per cent tin.

Tin alloys readily with both lead and iron, and hence fulfils the condition necessary for a binder for a lead coating on iron. With lead, tin forms a simple eutectiferrous series of alloys; the eutectic contains 63 per cent of tin [G 1] and melts at 182° C. Recently it has been shown [G 10] that the solid solubility of tin in lead is much less than formerly supposed; it varies from 2 per cent at room temperature to 18 per cent (approximately) at 150° C. The alloying of tin and iron has previously been discussed.

The manufacture of terne-plate follows quite closely that of tin-plate. Much of the light-coated product is made by means of a machine identical in all essential respects to that used for tin-plate of coke grade, the flux used being zinc chloride. The speed at which the sheets are passed through must be reduced in order to obtain as thick a coating as possible, and a higher temperature is required in order to maintain the bath in a molten state. In order to obtain a coating heavier than 15 pounds per base box, redipping of the sheets after they have passed through this machine is necessary.

A great deal of terne-plate, however, is still made by a process quite

similar to the hand-dipping process originally used for tin plate. The essentials of the process, as given by Camp and Francis [G 17] are as follows: The clean sheet after the final pickling is kept under water until ready to be immersed in a bath of hot palm oil. After a period of about 20 minutes in the oil, it is immersed in a bath of molten "terne" alloy which is kept covered with an oil layer. From here the sheet is passed into a second pot of molten metal and kept for several minutes. Upon removal from the second pot, the sheets are examined and cleaned, if necessary, before they are dipped into a third pot of metal, this one being of the highest purity of the three used. The sheets are then transferred with as little delay as possible to a bath of hot palm oil where they are allowed to "sweat", the sweating period being determined by the weight of coating desired. If left too long in the hot oil the coating may be entirely sweated off. The sheets are finally cleaned as in tin-plate manufacture in a branning machine. They are finished with either an oil or dry finish. A terne coating, on account of the lead contained, does not have the bright finish of tin plate no matter how much it may be polished.

During the solidification of the coating, a characteristic surface network or crystal pattern is formed which is analogous to the spangle on zinc-coated sheet. This appearance is known as "mottle" and the size of the network increases with the thickness of the coating. It serves a rather useful purpose, therefore, as an index of the weight of coating.

The finished sheets are carefully inspected and graded. Since a greater part of commercial terne-plate is used for roofing and similar purposes for which it is usually necessary to use the entire sheet, without cutting it, very close inspection and grading are necessary. The "prime" sheets must be free from all visible defects and even in the "menders" only such defects as can be remedied by redipping the sheet are permitted. The sheets of the "stripper" grade correspond to the seconds in tin-plate. They may be rerun and converted into primes having a lighter weight coating. The sheets of "scrap" grade are of no practical use.

The weight of coating on terne-plate is expressed in a manner similar to that used for tin-plate. In this case the base box consists of 112 sheets, 20 by 28 inches. The weight of coating varies according to the grade, from 8 to 40 pounds per base box. The following weights of coating have been recently agreed upon by manufacturers, distributors and users [G 21]: 8, 15, 20, 25, 30, 32 and 40 pounds per base box; the two weights, 12 and 35 pounds per base box, formerly used, being discontinued.

Most of the sheets used for making terne-plate for roofing purposes are either of the IC weight, approximately 30 U. S. standard gage, or IX which is approximately 28 gage in thickness. In the agreement mentioned above it was recommended that no terne-plate lighter than IC in thickness henceforth be manufactured for roofing purposes in the 28 by 20 inch sheets, commonly termed "short ternes".

The use of terne-plate for other uses than roofing has recently increased greatly. The material is admirable for deep stamping operations and nearly 40 per cent of the amount manufactured now is used in this manner [G 17]. Large quantities are used in the manufacture of gasoline tanks. Sheets much larger and heavier than the roofing size are manufactured for such purposes. They are known as "long ternes" by the trade.

Coatings of lead or of lead-rich alloys afford only a mechanical protection of iron against corrosion. Terne-plate of the heavier weights of coating, for example, 25- to 40-pound coatings, however, gives very satisfactory service as roofing material. It is necessary that such roofs be kept painted. The excellent paint-holding properties of such coatings compensate for some of the possible shortcomings which might be expected of coatings of this kind. The resistance of lead coatings to corrosive attack by sulfuric acid also makes them valuable for service for which coatings such as zinc are entirely unsuited.

Electroplated Lead Coatings.

The commercial application of lead plating is quite limited. Most of the practical applications of this type of protective coating depend upon the resistance of lead to attack by sulfuric acid. The usefulness of such coatings for protecting steel against an attack of this kind as well as from some of the special chemicals developed for chemical warfare was strongly emphasized by experience during the recent war [G 25, G 26, N 21], although very considerable study of lead plating has been done before that time [G 23, G 24].

Lead-plating baths.—Lead can be deposited electrolytically rather easily from a number of solutions but, largely on account of its tendency to form "trees" when deposited from certain solutions, the baths used commercially are limited to three [N 21] which are rather complex in their composition: the fluosilicate, the fluoborate, and the perchlorate solutions of lead. An addition of some substance such as glue is practically always necessary in order to ensure a dense impervious coating. Frölich and Clark [G 34] place the common lead-plating baths in the following order with respect to their tendency to form "trees",

the last solution being the best: acetate, nitrate, fluosilicate, fluoborate and perchlorate.

Applications of lead plating.—The most important single commercial application of lead plating is for the fittings of storage batteries.

Lance [G 33] has recently described a method for lead-coating steel pipe and sheet which, he states, has been used with success in service where resistance to sulfuric acid was an important feature, such as pipes buried in "fills" of cinders and ashes and for general usage in railroad shops. The method described consists in plating the pipe or sheet, which must be scrupulously clean, (1) by simple immersion in a solution of lead acetate followed (2) by electroplating in a second acetate bath containing some additions. Lead-coated rivets may be used for riveting plates together.

Lead plating has also been recommended [G 27] for lining the copper shells of the ordinary hand fire-extinguisher, for lining flues for conducting the waste gases from gas heaters, as a lining for brine containers and for any chemical equipment in which a sheet-lead lining cannot be attached.

Since lead coatings are used as a protection against severe chemical corrosion, it is necessary that they be considerably thicker than most other electroplated coatings usually are. Blum and Hogaboon [N 21] have recommended a minimum thickness of 0.003 inch (0.075 mm.). If lead coatings show evidence of being slightly porous, they may be improved very materially by slightly working or burnishing the surface. Lead-coated materials will withstand very severe deformation without any noticeable injury to the coating resulting.

Structure of lead coatings.—On account of the difficulties involved in preparing sections for metallographic study, no microscopic studies of the structure of lead coatings that throw any light on the structure of such coatings are available. Recently it has been reported [G 34] that when lead is electroplated upon platinum the atoms of lead take the lattice spacing of the platinum. This has not been confirmed, however.

Lead-tin Alloy Coatings.

In a fluoborate solution the potentials of tin and lead are not very different, hence the simultaneous deposition of the two metals, in the form of an alloy, from such a solution containing both tin and lead can readily be accomplished [G 31]. Such coatings have a much finer structure than a coating of either lead or tin alone deposited from a fluoborate solution, and by the addition of glue the coating can be made still finer-grained. Aside from a special application of this coating by

the U. S. Navy Department, the electrodeposited lead-tin alloy coatings do not seem to have been used commercially.

Cadmium Coatings.

Agreement as to the true position of cadmium in the electrochemical series of metals, particularly the relative position of iron and cadmium, has not yet been reached. The position of cadmium given in Table 1, however, agrees with observations made on the protective action of cadmium coatings on iron or steel exposed to atmospheric and to accelerated corrosive conditions [H 10, H 11] and, in all probability, is correct.

Cadmium coatings are applied on a commercial scale only by electroplating. They may be applied by the metal-spraying process but the high cost of the cadmium wire necessary for carrying out this process has not encouraged the development of cadmium coating by this method. The electrodeposition of cadmium was undertaken, with considerable success, as early as 1849 [H 1]. It is only recently, however, that cadmium electroplating on a commercial scale has been attempted. It is of interest to note that the solution first used for cadmium plating, cadmium carbonate ($CdCO_3$) dissolved in a solution of sodium cyanide (NaCN), is of the same general nature as those used in commercial cadmium plating today.

Cadmium coatings will take a high polish and are much more pleasing in appearance than are those of zinc. Thus they combine, to some extent, some of the attractive appearance of nickel coatings with the protective value of zinc coatings. Since cadmium stands closer to iron than does zinc in the electrochemical series, it may be predicted that the life of a cadmium coating when applied to iron should be considerably longer than one of zinc of the same weight under the same service conditions. Zimmerman and Irwin have stated, on the basis of the results of an investigation by the Army Air Service [H 10], that cadmium coatings 0.0003 inch thick are equivalent, in the protection afforded to steel, to zinc-plated coatings 0.001 inch thick for ordinary conditions of exposure. It would seem, therefore, that cadmium should be distinctly superior to zinc for coating threaded articles or parts which must fit very accurately when assembled.

On the other hand, it has been pointed out that, on account of the smaller potential difference between cadmium and iron as compared to the potential difference between zinc and iron, cadmium would not be expected to exert a protective action over as large an area as zinc [N 21], hence the need for a more impervious coating in the case of cadmium. Reliable published information concerning the service behav-

ior of cadmium coatings is very meager, however. In one American patented process for cadmium plating, the plated articles were given a baking treatment for several hours at a temperature somewhat below 200° C. Zimmerman and Irwin concluded that no advantage was gained by such treatment so far as corrosion resistance was concerned. Desch [H 9] has investigated the use of cadmium coatings on aluminum and concluded that it is one of the most desirable of the metallic coatings for this purpose but that there are other types of coatings which are much more suitable, on the whole, for protecting aluminum.

Desch also concluded that a preliminary coating of cadmium improved the character of a nickel coating applied to aluminum very materially. The advantage of using cadmium as the first coat applies also in the nickel plating of iron and other metals. Although it has not been used to any great extent for this purpose, cadmium appears to have distinct advantages over the other metals ordinarily used under nickel [N 21].

Aluminum Coatings.

From the relative position of aluminum and iron in the electrochemical series (Table 1) it might be concluded that, provided such coatings could readily be applied, aluminum should be a very desirable coating metal for the protection of iron and steel against atmospheric corrosion. Such a conclusion is not fully supported, however, by the behavior of such coatings in service. On account of the protective oxide film which readily forms on a fresh surface of aluminum upon exposure to the atmosphere, the anodic behavior of such a coating toward iron is almost entirely masked and the coating is essentially neutral in its electrochemical behavior toward iron. The most important application of aluminum as a coating metal is for the protection of metals, particularly iron and steel, when exposed to elevated temperatures.

Coatings of aluminum may be deposited by hot-dipping, by cementation and by metal-spraying. The electrodeposition of aluminum is not practicable. Coatings of aluminum paint have many of the properties of true metallic coatings. When such a paint is applied to a surface, the aluminum pigment, which is metallic aluminum in the form of tiny flat scales, shows a decided tendency to collect at the surface of the paint film and to "leaf" together. Thus, in effect, a continuous metal film is formed, differing from ordinary metallic coatings, however, in that there is no metallic bond between it and the base metal. The paint vehicle forms the bond for the coating.

HOT-DIPPING.

Aluminum alloys very readily with iron, hence the fundamental condition for successful coating by hot-dipping is fulfilled. Iron and aluminum are completely miscible in the molten state. In the aluminum-rich mixtures, the iron precipitates from the solution, upon solidification, as the compound $FeAl_3$ (41% iron). The temperature at which this compound forms is only very slightly below the melting point of

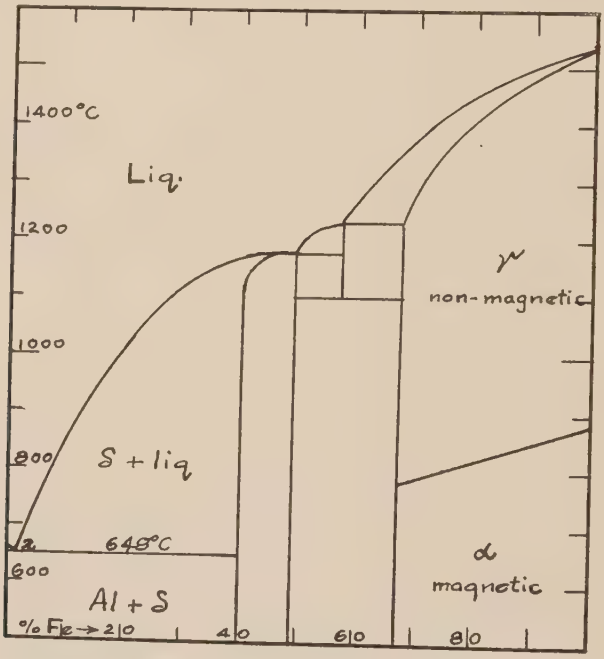

FIG. 53. Equilibrium diagram of aluminum-iron alloy system (International Critical Tables vol. 2, 1927).

There is still some uncertainty concerning the central portion of the diagram.

aluminum (657.7° C.). The solubility of iron in solid solution in aluminum is almost nil. Aluminum-rich alloys of the series, up to 41 per cent of iron, have a structure consisting of a matrix which is essentially pure aluminum, embedded in which is a hard brittle constituent, the compound $FeAl_3$. On the other hand, aluminum is readily soluble in solid solution in iron. The recent work of Kurnakow and his co-workers [I 12] shows that as much as 35 per cent of aluminum can be retained in solid solution in α-iron which is greatly in excess of what has been reported by previous investigators of the iron-aluminum alloy systems. These features are shown in the equilibrium diagram of the

iron-aluminum series (Fig. 53). All of the features of the diagram, especially in the central portion, have not been established with certainty as yet.

Success in the hot-dipping of iron in aluminum is attained with difficulty and only after special preparation of the surface of the iron. Much of the difficulty is to be attributed to the tenacious film of aluminum oxide which forms so readily, as well as to the large amount of iron-aluminum compound which forms. If the iron or steel, after suitable preliminary cleaning, is dipped in a bath of molten tin, however, prior to its immersion in the molten aluminum or aluminum alloy, the resulting coating is very greatly improved [I 1]. Although aluminum-coated iron and steel, hot-dipped in this manner, is quite resistant to atmospheric corrosion, the material is not used, as such, to any very appreciable extent, but is employed in the calorizing process described below [I 7, I 11].

Calorizing.

Calorizing is the commercial name for the cementation of a metal surface by means of aluminum. The process was developed at the Research Laboratory of the General Electric Company and is intended primarily as a means of protecting iron from oxidation at elevated temperatures rather than from the more familiar type of corrosion.

The method is quite similar to that of sherardizing. The articles to be treated are packed in a drum in a mixture of powdered aluminum, aluminum oxide and a small amount of ammonium chloride. The drum is slowly rotated as it is being heated and an inert atmosphere, usually of hydrogen, is maintained within it. Ruder [I 3], in his description of the process as first developed, stated that the aluminum content might vary from 5 to 50 per cent according to the service to which the treated piece was to be put and that about one per cent ammonium chloride was needed. For steel and iron a calorizing temperature of 900° to 950° C. was recommended, and for copper and brass parts, 700° to 800° C. The purpose of the alumina was to prevent coalescence of the particles of aluminum as the temperature used is very considerably above that of the melting point of aluminum (658.7° C., 1218° F.). A hydrogen atmosphere was maintained within the container during the entire period. The aluminum and the chloride must be renewed from time to time as the mixture is used. Martin [I 19] recommended, as a result of his recent study of the calorizing process, a mixture consisting of 50 per cent (by weight) aluminum, 45 per cent alumina, and 5 per cent ammonium chloride as being very useful for most purposes, and reports that a temperature of 875° C. (1600° F.)

gave quite satisfactory results, at least on a laboratory scale. Martin also obtained good results by carrying out the process in an atmosphere of illuminating gas.

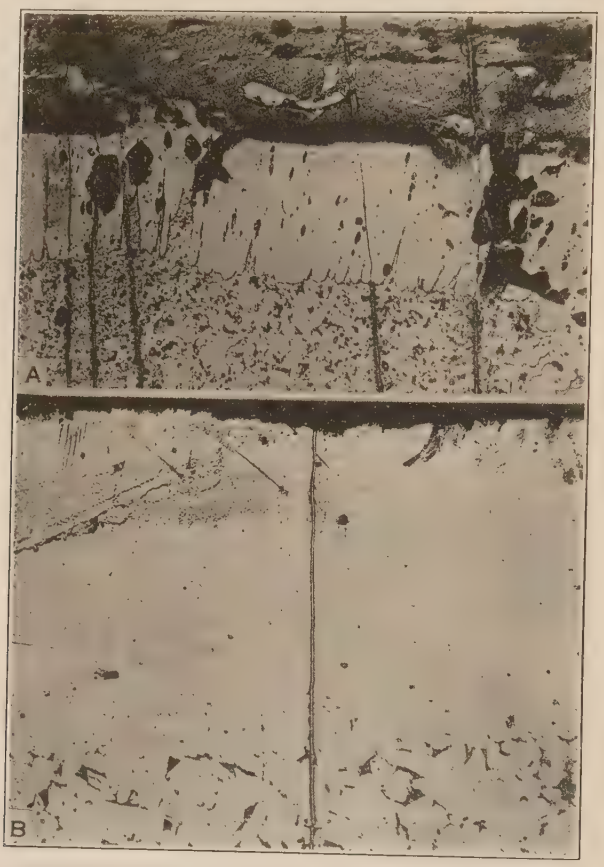

FIG. 54. Structure of an aluminum coating on steel, × 100. Etchant, alcoholic solution of nitric acid.

A, The coating was formed by dipping in molten aluminum and consists of two layers, an outer soft one of aluminum (upper part of the micrograph) and a hard alloy layer adjacent to the steel. The scratches were drawn for the purpose of showing the relative hardness of the layers.

B, Coating on a steel rod "calorized" by the commercial powder method. The coating consists of a solid solution of aluminum in iron. By heating *A*, a coating similar to *B* would be produced.

It has already been mentioned that the hot-dipping method is now utilized in the calorizing process [I 11]. If metals which have been coated by dipping in aluminum are heated, the aluminum diffuses into the underlying metal so that a coating results which is essentially the

same as one produced by the older calorizing method. Such coatings are much thinner than those made by the older method but have the advantage of being considerably cheaper. They are intended primarily for small articles and especially for pieces of small cross section.

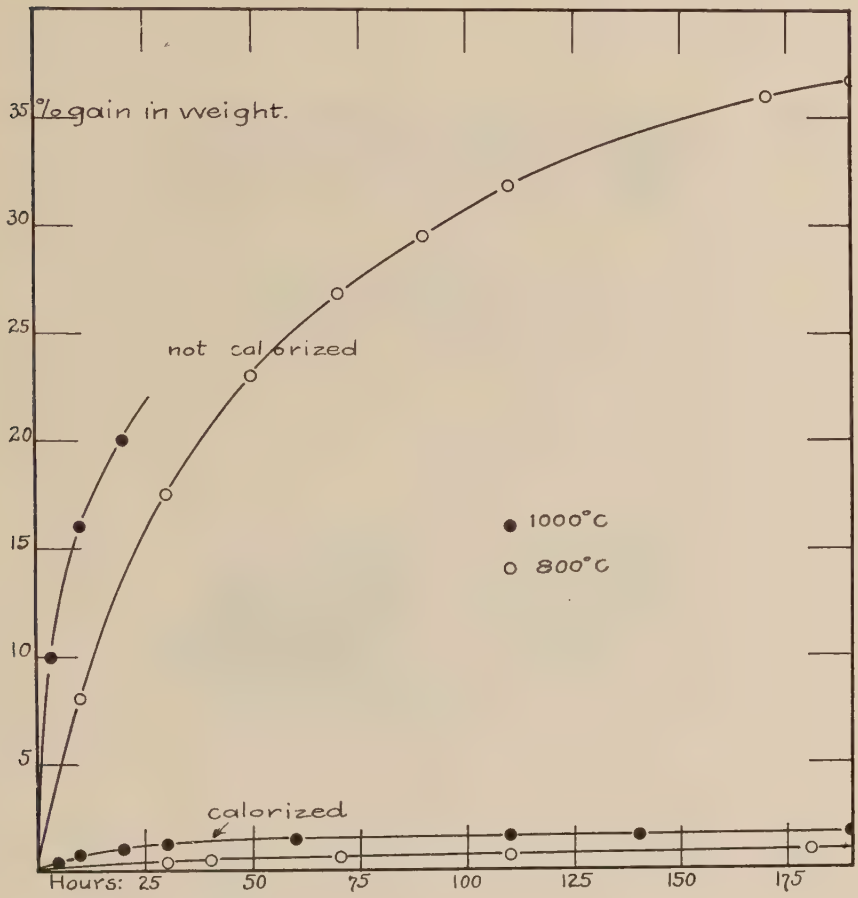

FIG. 55. Rate of oxidation of calorized and uncalorized iron [I 3].

Properties and uses of calorized coatings.—The aluminum which is deposited during calorizing upon the surface of the treated metal alloys with the second metal [I 3]. The outer hard rough porous layer of the coating formed, according to Martin [I 19], consists largely, in the case of iron, of the aluminum-rich compound $FeAl_3$ and, on account of its porosity, affords little if any protection to the treated metal. Beneath the outer layer is one which is considered to be a solid solution

of aluminum in the base metal. The structure of this layer is shown in Figure 54. It is to this layer that the characteristic behavior of a calorized metal is to be attributed.

The calorizing treatment is especially to be recommended as a protection against oxidation at high temperatures. Figure 55, giving results reported by Ruder, shows the very decided difference in the rate of oxidation of iron in the treated and the untreated condition at 800°

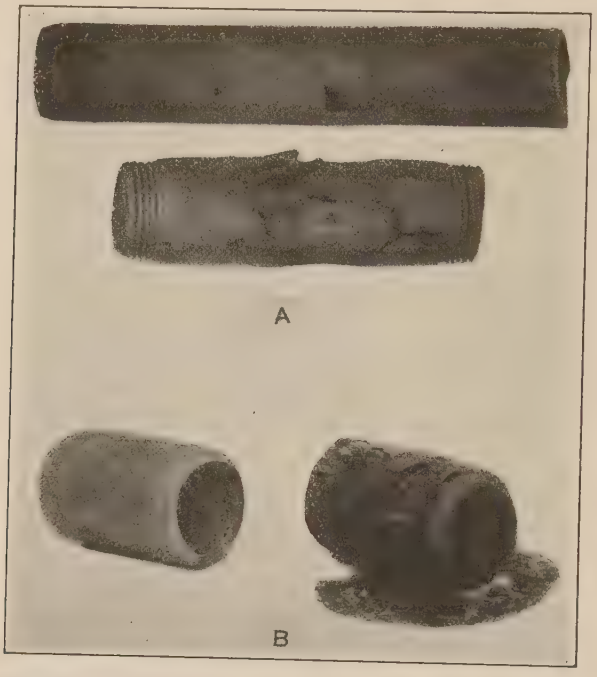

FIG. 56. Appearance of calorized and uncalorized steel pipe after heating [I 2].
A, 900°C (1652°F), 8 hours.
B, 800°C (1472°F), 100 hours.
The uncalorized pipe in each case shows pronounced scaling.

and 1000° C. (1470° and 1830° F.). Figure 56, from Allison and Hawkins [I 2] shows the appearance of calorized and uncalorized iron tubes after heating.

Most of the resistance to oxidation at high temperatures shown by a calorized metal can be attributed to the tenacious coating of aluminum oxide which readily forms in the early stage of the heating and prevents further oxidation of the underlying metal. The calorized coating when first put on is quite thin, being only 0.001 to 0.004 inch in thickness [I 3]. Upon heating, however, the aluminum diffuses deeper

into the metal and the coating becomes thicker but, of necessity, of a lower average aluminum content. This fact is of importance as it limits the temperature at which calorized metals may be used to best advantage. If the outer protective layer of alumina becomes broken after the article has been used for a time it cannot be renewed, as the aluminum content of the underlying layer has been lowered too much as a result of diffusion and deterioration of the entire article will result in a short time.

According to Cournot [I 26], the life of calorized iron below 900° C. (1650° F.) should be almost unlimited; if used at 900° to 980° C. (1800° F.), the probable maximum life will be 20 times that of an untreated piece, while if the service temperature is from 980° to 1100° C. (2010° F.), the life may be 5 times that of an untreated piece. Howe and Brophy [I 11] also place 900° C. as the maximum temperature to be used in order to obtain long life with calorized iron.

Calorized coatings made by the dipping method are not intended for very severe service. The calorizing process should be applied to the finished piece. On some metals, for example, nickel, the coating is hard and somewhat brittle. None of the metals after treatment will withstand severe deformation without damaging the coating.

The mechanical properties of the treated metal are, as a rule, not affected in any way other than what is to be expected as a result of heating the metal for the 2 or 3 hours required at the calorizing temperature. The results given by Farr [I 7] (Table 15) show the tensile properties of a soft steel tube after treatment.

TABLE 15.—TENSILE PROPERTIES OF SOFT-STEEL TUBING AFTER CALORIZING[1] [I 7].

Specimen	Yield Point	Ultimate Tensile Strength	Elongation		Reduction of Area
			2 In.	8 In.	
	Lbs./Sq. In.	Lbs./Sq. In.	Per Cent	Per Cent	Per Cent
1 *	29,650	47,150	...	...	51.5
2	28,750	45,300	30.5	23.0	43.0
3 **	26,300	49,000	12.0	...	46.5
4	27,450	46,200	40.5	29.0	40.5
5	24,750	46,400	38.0	27.0	50.0
6	24,700	40,050	46.0	29.5	60.0

[1] The values have been "rounded off" slightly from those given by Farr.
* Punch marks pulled off.
** Broke in grips.

Calorized coatings have proved to be quite resistant to attack by sulfurous gases and hence such materials have found an important application in the oil-refining industry [I 24], such as tube stills for cracking

and topping as well as valves, retorts, and condenser parts. In addition to its use for furnace parts such as conveyers, stokers, roasters, rotary dryers, kiln parts, carburizing and heat-treatment boxes, and pyrometric equipment, important applications are being made [I 7] in Diesel engine construction, in the carbon and coke industry, as well as many relatively minor miscellaneous uses where resistance to oxidation and sulfur attack at high temperature is the important factor to be considered.

Modifications of the calorizing process.—In addition to utilizing the hot-dipping process as a part of the calorizing treatment, various other modifications have been proposed. Martin [I 19] concluded, as a result of his investigation of the method, that essentially the process consists in the use of aluminum and a chloride which is volatile at the temperature employed. He has described a process depending upon the reaction, $AlCl_3 + Fe \rightleftarrows FeCl_3 + Al$, which gives coatings which are essentially the same in appearance, structure and properties as those made in the regular manner. If the containers used in this modified process as well as in the regular calorizing process are luted so as to be fairly air tight, Martin concluded that the use of a hydrogen atmosphere was not necessary but that the process could be carried out in a manner analogous to the carburizing of steel. The chloride used, when volatilized, maintains the inert atmosphere needed within the container enclosing the mixture and parts which are to be treated. Cournot [I 26] has investigated the properties of coatings made by using an aluminum-iron compound of the approximate composition, $FeAl_3$, as proposed by Meker, and concluded that the coatings produced are very comparable with those made in the regular manner from powdered aluminum. The cost of preparing this alloy in powdered form is very much less than that of making the powdered aluminum. According to Kayser [I 23], however, it is not necessary that the aluminum be in powdered form but that the "swarf" resulting from the grinding or sawing of aluminum may be used. The action is considerably slower in such a case, however, than when the powdered metal is used [I 19].

Considerable advantage may be gained by spraying with aluminum, by the metal-spraying process, parts to be used at high temperatures, such as furnace grate bars, according to Hopfelt [I 20].

Fisher and his co-workers [I 6] have reported that a resistant coating can be built up by means of an aluminum paint. In the experiments reported, the surface to be protected, after cleaning, was painted with aluminum suspended in a solution of rosin in benzine and then heated in an open flame. By repeating this process several times, it

was reported that a coating which was quite resistant at elevated temperatures was built up. In all such modified processes as this, the protection of the iron is gained in essentially the same manner as in the calorizing process.

Mechanical Aluminum-coating Process.

Sheet steel coated with aluminum by a mechanical or "welding" method has been produced but is not a commercial product. The aluminum layer is always relatively thick and material of this kind has

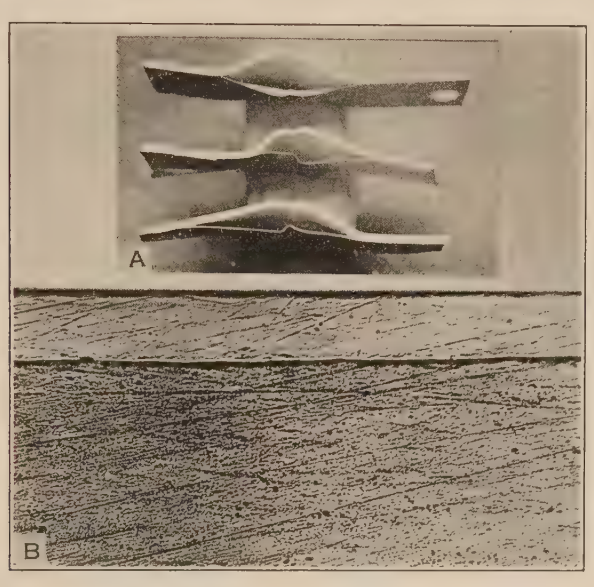

Fig. 57. Aluminum coating on steel, prepared by a mechanical process.
A, Note how the coating stripped from the base on bending, × 1.
B, Coating of *A*, × 100, unetched. Note the alloy layer adjacent to the steel. This was responsible for the separation upon bending.

shown high resistance to accelerated corrosion tests. The rapid alloying action occurring between the two metals, however, usually results in a very brittle layer adjacent to the steel or iron base, and the uses to which such material could be put would be limited to those which did not involve bending or any other severe deformation. Figure 57 shows how readily such a coating may be stripped from its base.

Recently it has been shown that duralumin may be very effectively protected against corrosion by a coating of aluminum applied by the mechanical coating process. Aluminum alloys of the duralumin type are important engineering materials, especially in aircraft construction, since very high tensile properties can be developed for such materials

by heat treatment, thus combining lightness with high strength. The tendency of such material, especially in thin sheet form, under some conditions, to become embrittled as a result of corrosion has limited the use of such materials somewhat. It has been shown that a coating of aluminum very effectively protects duralumin against deterioration by corrosive attack.

Chapter 11.

Gold and Silver Coatings.

History of Gilding and Silvering of Metals.

Historically, the first metal coatings were those of gold and silver. Although the idea of ornamentation was always foremost in the minds of the users of such coatings and still remains so, they are, nevertheless, properly to be considered as protective coatings. At the present time gold and silver coatings are used in some instances, although to a very limited extent, primarily as a protection against severe corrosive attack; typical examples are the silver lining of autoclaves, the gold plating of the interior of bomb calorimeters and the gold plating of standard weights and other laboratory equipment. The silver plating of the fixtures used for dispensing soda water and similar drinks is an example of the use of silver plating on a larger scale.

The gilding and silvering of metals has been practiced for centuries and many ingenious methods were developed. The earliest method depended upon the use of gold hammered into foil. This practice was known in Egypt as early as 3000 B.C. Gilding and bronzing by means of finely powdered metal in suspension in a suitable vehicle followed. Fire- or amalgam-gilding, which was applicable to silver as well as to gold, was known, at least in a crude form, as early as 300 A.D. [J 3]. In this method the surface to be coated, which was usually brass or copper, was first treated with a solution of mercurous nitrate and then rubbed with an alloy consisting of 9 parts of mercury to 1 part of gold. After the surface had been thoroughly amalgamated, the mercury was expelled by means of heat. This could be repeated more than once if a very heavy coating was desired. The use of the mercury insured intimate alloying between coating and base. It is claimed by some that such coatings are much superior to the modern electroplated gold coatings, and the process is still used to a very limited extent.

The method of "close plating" [J 14] was formerly widely used for producing silver-coated articles and was the immediate predecessor of the fusion method which we know principally as the method for making "Old Sheffield Plate."

In close plating, the finished article was cleaned with ammonium

chloride and then dipped into molten tin. A thin foil of silver cut to the approximate size and shape needed was carefully fitted over the article and a hot soldering iron lightly rubbed over it. The tin melted and soldered the silver coating in place after which the article was burnished and polished. Close plating was applied to articles of rather complex shape including knives, forks and spoons and other tableware as well as buttons, buckles, snuff boxes, spurs and other articles for personal adornment. Close-plated articles could not be heated, otherwise the tin solder would melt and the coating strip off. Neither would it withstand very severe corrosive conditions, as blisters formed as a result of corrosive attack beneath the coating. The method is still in use today, however, in a few special cases.

The fusion method of silver plating of copper was discovered by Thomas Boulsover about 1743 [J 14]. In brief, this consisted in heating nearly to the fusion temperature of silver, a slab of copper with a thinner plate of silver in close contact with it, on the side which was to be plated, together with the subsequent rolling of the composite slab into sheet form. First of all, the slab which, though described as copper, was an alloy of copper with some zinc and lead, was planed off to a very smooth surface as was likewise the silver plate, the thickness of which depended on the final thickness of silver plating desired. For double-coated sheet both sides of the copper slab were treated. The copper slab and silver plates were pressed firmly together, covered with sheet copper which had previously been dressed with powdered chalk to prevent it from fusing to the silver, bound with iron wire and heated until the silver began to "weep." It was then removed from the furnace and after cooling the surrounding sheet was stripped off and after being cleaned, it was ready to be rolled into sheet form. From this composite sheet many intricate and complex shapes were worked out which are known to us as "Old Sheffield Plate". With the discovery and commercial development of the cheaper electrolytic method of silver plating, the fusion method passed out of use.

Electroplated Silver Coatings.

The commercial application of the electrodeposition of silver dates from about 1840 with the discovery by John Wright, a young surgeon of Birmingham, England, that a cyanide solution of silver must be used in order to obtain a dense, uniform adherent coating of silver [J 6]. Cyanide solutions are still used today, practically exclusively in the silver-plating industry. Another important fact concerning silver deposition, that is, that whereas the deposit obtained from an ordinary cyanide bath has a "frosted" appearance, bright deposits can

be obtained by the addition of a little carbon disulfide to the plating bath, was also made very early in the history of the industry (1847). Numerous variations in the preliminary treatment of metals to be plated, such as "strikes" and "dips" in various solutions, before immersion in the plating bath are necessary. Aside from development of the technique of the industry, no pronounced changes have been made for many years.

Thickness of Silver Plating.

It was formerly the custom in describing silver-plated ware to use such designations as "triple plated", "quadruple plated" and the like. The use of these misleading terms has now been discontinued by American manufacturers and the weight of silver, for example, per unit of surface area as on a stated number of articles of similar kind and size, is used instead to indicate the thickness of the coating. Table 16 gives the average thickness of the coating on silver-plated tableware as recommended in a specification recently promulgated by the Federal Specifications Board [J 13].

Table 16.—Recommended Average Weight of Coating on Silver-plated Tableware [J 13].

Articles	Thickness of Silver Coating	Weight of Silver
	Inch	Dwt./Sq. Ft.
Flat ware[1] for frequent use	0.0008	12.8
Hollow ware[2] for frequent use	0.0008	12.8
Flat ware[1] for occasional use	0.0006	9.6
Hollow ware[2] for occasional use	0.0006	9.6

[1] Knives, forks and spoons.
[2] Pitchers, trays, tureens, dishes and covers, bowls, coffee pots and the like.

It is also necessary to take into account the thickness of the coating on those portions of plated tableware which are subjected to the greatest wear, such as the back of the bowl of spoons or the tines of forks. It is common practice, for the better grade of tableware, to use a heavier coating on such portions. This is obtained either by the use of a silver insert in the "blank," which is later plated, or by a supplementary plating of the desired portions after the article has been given the regular plating. The specification referred to above requires the silver coating to be 0.0012 inches thick on such spots.

Defects in Silver Coatings.

The occurrence of red stains on silver-plated articles is sometimes the cause of considerable concern to silver platers. This defect has

been shown [J 10] to arise during the polishing operation and appears to be related to the improper use of the polishing rouge on a surface while still heated by the polishing operation.

"Spotting out" on silver-plated surfaces is another defect. According to Burgess and Richardson [J 4] these white spots which do not appear until some time after the article has been removed from the plating bath are to be ascribed primarily to inclusion of some of the cyanide in the coating. The exact nature of the defect, however, has not been fully established.

At times difficulty is experienced in the polishing of silver coatings. The coating in such cases often has a coarse crystalline appearance which is removed with difficulty by ordinary polishing methods. It has been reported that silver may be electrodeposited under certain conditions so that the crystals of the silver form as extensions of the pre-existing crystals of the nickel-silver base metal (compare Fig. 48). Such coarsely grained silver coatings cannot be satisfactorily polished by the methods usually employed. It has not been established, however, that this is the only cause for irregularities in the polishing of silver-plated coatings.

Tarnishing of Silver.

Although silver does not oxidize under ordinary conditions it is quite readily converted to sulfide. The tarnishing of silver is the result of the formation of silver sulfide either from hydrogen sulfide gas or from sulfur-bearing organic compounds in certain foods. Dry hydrogen sulfide gas has only a very slight effect. The presence of moisture or of an acid, such as sulfur dioxide, greatly accelerates the reaction [J 11]:

$$2Ag + H_2S \rightarrow Ag_2S + H_2.$$

The removal of the tarnish film may be done by polishing the surface with a fine abrasive or by electrolysis. The latter is a means by which the reaction expressed above is reversed, the silver sulfide being changed to metallic silver. If, in a solution of sodium chloride and sodium carbonate, both of which are common household materials, the tarnished silver is placed in contact with a metal such as zinc or aluminum, the detarnishing process will proceed of its own accord. The zinc or aluminum functions as the anode, the silver as the cathode, and by means of the "cathodic" hydrogen the silver sulfide is reduced to silver.

$$Ag_2S + 2H \rightarrow 2Ag + H_2S.$$

There is no appreciable loss of silver by this process. Theoretically there should be none whatever. If the silver has been very severely

tarnished, the surface after cleaning is dull on account of the thin film of "moss" silver formed by the reduction of the sulfide. Buffing may be necessary in such cases in order to restore the polish. Ordinarily, however, this is not required.

Attempts have been made to improve the properties of electroplated silver, particularly its resistance to tarnish, by the simultaneous deposition of another metal along with it. Cadmium has been used commercially to a limited extent for this purpose and superior tarnish-resistance has been claimed [J 7] for the silver-cadmium alloy deposit. In a recent investigation, Aten and van Putten [J 12] have shown, however, that in such alloys a cadmium content of 3 per cent or more imparts an undesirable yellowish tinge to the coating. They also concluded that under the ordinary conditions of silver plating the amount of cadmium deposited is too small to be of any real significance.

Gold Coatings.

Electroplating Gold.

Gold plating is carried out in a variety of ways [J 2]. From cyanide solutions the plating is done by use of an external source of electromotive force; the article to be plated is made the cathode of the electrolytic cell and the anode is of gold. By varying the composition of the plating solution, it is possible to obtain coatings of different colors; green, red, and white gold as well as the usual color may be readily obtained. The special golds are in reality alloys formed by the simultaneous deposition of gold with another metal; silver in the case of green gold, copper for red gold, and nickel for white gold.

Gold can also be plated without the application of an electromotive force external to the plating cell. One such method merely requires the setting up of a primary battery which uses two solutions; one of them, the gold solution, kept separate from the second one, sodium chloride, by means of a porous cup. A strip of zinc, the anode of the cell, is immersed in the sodium chloride solution; the article to be plated, either brass or copper, is hung in the gold solution within the porous cup. Electrical contact by means of a wire is made between the two electrodes, that is, the zinc strip and article to be plated. In such a cell, gold from the solution deposits upon the surface of the cathode (article to be plated) when a current is allowed to flow by connecting the anode and cathode by a wire. The deposit is very uniform and adherent. A much simpler method merely requires the immersion of the article, brass or copper, in a gold solution of the proper composition. In this case, the article is plated by a slight amount of copper or zinc passing into solution and precipitating an equivalent amount of gold on the

surface. The coating obtained is very adherent but exceedingly thin and the method is used only for small cheap articles. Such coatings are only a few millionths of an inch in thickness [N 21].

Gold-filled Plate.

"Gold-filled" articles, such as watch cases, are stamped from a gold-plated sheet which is made in a manner very similar to that described above for old Sheffield plate. In the case of the gold-plated sheet, however, a thin sheet of "brazing" alloy is inserted between the slab of nickel-silver or brass used as the base metal and the overlying sheet of gold. It is necessary to heat the material only above the melting point of the braze used which is considerably lower than that of either the gold or the base metal.

According to a decision, January 25, 1923, of the U. S. Federal Trade Commission relating to the gold-filled watch case industry, the minimum thickness of the gold layer on such gold-filled plate must be 0.003 inch on the outside of the case and 0.001 inch on the inside.

By the use of proper reducing solutions gold and silver can be reduced to the metallic form from their solutions and coatings obtained directly by this means [J 2]. This method is used principally for the production of mirrors, however, rather than for coating other metals.

Chapter 12.

Miscellaneous Finishes.

Most of the attempts to produce protective coatings on iron or steel by chemical treatment of the surface are based upon oxidation of the metal surface. The term "inoxidation" is frequently used in referring to these processes.

Comparatively recently it has been found that the composition of a steel influences decidedly the physical character of the oxide which forms naturally when the steel is allowed to corrode under atmospheric conditions. Thus, the presence of a small amount of copper in low-carbon steel or in open-hearth iron renders such a material more resistant to atmospheric corrosion when exposed in the bare state than is a similar steel or iron containing no copper [L 28, L 30, L 31]. Only a relatively small amount of copper is required to give the effect, a copper content of 0.15 to 0.25 per cent being usually considered sufficient. The coating of rust which forms on a copper-bearing steel sheet when allowed to corrode in the atmosphere is, as a rule, more adherent, denser and smoother than the rust coating which forms on a non-copper-bearing steel under the same conditions [A 25, p. 108]. The difference in the rate at which the two materials, copper-bearing and copper-free steel, corrode when exposed freely to the atmosphere is undoubtedly, therefore, largely the result of this difference in the character of the rust coating on the two materials.

The coatings obtained by chemical treatment of a metal surface vary widely in their protective value. None of them protects the underlying metal other than in a mechanical way. Many are merely of the nature of a finish or surface coloring and are used admittedly with ornamentation and finish as the principal reason for their use. Others are thick enough so that they afford very considerable protection and, since many of them are oiled in order to produce an attractive appearance, the degree of protection is increased very considerably.

Methods of Producing Oxide Coatings.

Heating.

The principal difficulty to be overcome is to control the oxidation so as to obtain an adherent coating. The black or magnetic oxide,

Fe_3O_4, is the one desired; the ferric or red oxide is often pulverulent in character and worthless as a coating.

Although it had been known since the work of Lavoisier in the latter part of the 18th century on the production of hydrogen that the action of steam on hot iron gives rise to a fairly adherent oxide layer on the iron, the first attempt to make any practical application of this fact was not till 1876 by Barff [L 1]. His process consisted, essentially, in heating the iron articles, cast iron, malleable iron, as well as wrought iron and steel, in an externally heated furnace into which steam was admitted at approximately 540° C. (1000° F.). The thickness of the oxide coating formed depended upon the duration of the process; usually a period of 6 to 18 hours was required.

The process described by Bower a few years later [L 2] grew out of an attempt to reduce the cost of the Barff process. Air, the amount admitted to the furnace being controlled according to the area of the surface to be treated, was used instead of steam, and a second or deoxidizing stage was introduced into the process, the purpose being to reduce the ferric oxide formed in the first stage to the magnetic oxide. The cost of the process was further reduced by introducing an internally heated furnace [L 3]. In practice all that was necessary was to regulate the amount of air required for burning the gas used to heat the furnace and the articles contained. In the first stage, a slight excess of air was used and in the second the air was shut off almost completely. After the purchase of the Barff patents, the two were combined as the Bower-Barff process which embraced the desirable features of both the former processes [L 5]. The articles were heated in an internally fired furnace, superheated steam (at 1000° F., 540 °C.) was then admitted into the furnace for half an hour or so, a hot reducing gas such as producer gas was next admitted for a short time, after which the cycle was repeated until the desired thickness of coating was obtained. In many cases the use of steam could be dispensed with. The process was formerly used much more extensively than it is at present.

Many attempts have been made to improve the Bower-Barff oxidation process, principally by shortening the period required for treatment. The process described by Weigelin [L 8, L 9] was very much like that of Bower and consisted in alternate exposures of the hot material to a reducing (smoky) and to an oxidizing flame, producer gas being used. In the Gesner process [L 7], the hot iron articles, after treatment, with the steam, were subjected to hydrocarbon vapors produced by injecting a small amount of naphtha into the furnace. In other modifications certain chemicals were used. A bath containing tin and

copper into which the articles were dipped before treatment in the furnace was the special feature of the Bertrand process [L 7, L 11]. In others, as the Bontempi [L 15] and the Swan method, the chemicals, which usually contained copper, were volatilized within the furnace. It was claimed that by such procedures the time required could be very materially shortened and the character of the coating improved.

No completely satisfactory explanation for this has yet been advanced. However, the similarity in the use of copper solutions in these oxidation processes and in the addition of a small amount of metallic copper to steel in order to cause it to form a relatively tough adherent oxide coating when corroded in the atmosphere suggests a common cause for these two phenomena. Posnjak [L 32] has shown that the rate of oxidation of a solution of a ferrous salt to the ferric condition is greatly accelerated by the presence of a very small amount of copper in the solution. It appears therefore that the superior mechanical properties of the iron oxide layer formed in the presence of copper are, perhaps, to be attributed in large measure to this accelerating effect of copper on the rate of oxidation of the iron. The iron may be considered as having been rendered to a slight extent similar to those metals which form a "self-healing" oxide film on any freshly exposed surface.

By means of x-ray examinations, Bozorth [L 26] has recently shown that an oxide coating made by the Bower-Barff or related processes consists of several layers which differ from one another in the degree of oxidation. He reported that the inner layer, the thickness of which for the particular specimen used was of the order 10^{-2} cm., was ferrous oxide, FeO; the intermediate one, 2×10^{-4} cm. thick, magnetite, Fe_3O_4; and the outer one, ferric oxide, Fe_2O_3, 2×10^{-5} cm. thick.

The corrosion-resistance of Russian sheet iron is to be attributed to the tenacious oxide layer covering such sheets. The characteristic "planished" appearance of such material resulted from the hammering to which the pile of heated sheets was subjected.

Satisfactory oxide coatings may be produced simply by heating if carefully done. The resulting coating is usually very thin and is primarily a finish rather than a protective coating. The surfaces to be treated should be polished and must be scrupulously clean. They may be heated in a muffle furnace or even in a sand bath [L 47]. A much better method is to heat in a bath of fused nitrates. The addition of a small amount of manganese dioxide to the bath improves the results [L 6]. This is the method commonly used for "bluing" steel [L 19].

The color of the oxide coating formed in this way varies according

to the temperature used as well as the period of heating. The colors obtainable, however, are limited to those shown in Table 17. They are usually referred to as "tempering colors". The results by Gale [L 21] (Table 17) show the thickness of such coatings as computed from the gain of weight of the steel article heated at different temperatures so as to produce the color indicated.

TABLE 17.—THICKNESS OF OXIDE COATINGS CORRESPONDING TO DIFFERENT TEMPER COLORS [L 21].

Increase in Weight	Color of Surface	Thickness of Coating [1]
Mg. per Sq. Meter		Cm.
6.6	Brownish white	4.2×10^{-7}
10.0	Bright brown	6.3 "
12.5	Dark brown	7.9 "
16.1	Red-brown	10.2 "
19.4	Red-brown	12.3 "
23.2	Purple	14.7 "
26.9	Dark purple	17.0 "
33.7	Dark violet	21.3 "

[1] Computed from the gain in weight, by assuming a density of 5.25 gms. per cu. cm. for the oxide layer, the density of ferric oxide.

OXIDATION BY IMMERSION METHODS; BROWNING.

The "browning" of steel may be taken as representative of the multitudinous emperical methods used for the coloring of metal surfaces [L 46, L 48, L 49, L 50, L 52]. The object in all such cases is primarily that of ornamentation and, although such coatings always afford some degree of protection, this varies very widely according to the thickness and uniformity of the coating which is built up.

The browning of steel may be considered as a controlled corrosion. Numerous solutions are used for the purpose, most of which contain ferric chloride; some contain a copper salt. Very satisfactory results can be obtained with a simple solution of ferric chloride in alcohol and water. All the solutions are decidedly corrosive toward iron and steel and the number of treatments required in any particular case depends largely upon the relative corrosive properties of the solution used.

The clean surface is first coated with the "browning solution" by swabbing or dipping and then dried; usually two applications are used. The articles are then held in a warm cabinet (60° to 80° C.) for somewhat less than half an hour and then transferred to the "rusting" cabinet in which the humidity is carefully controlled and should not be far below the saturation point. After a period of perhaps one hour or so, the articles have been rusted to a dirty red color, and are then held in a third warm cabinet to "set" the rust, although this is not always

considered necessary. They are then put into boiling water and heated for a quarter of an hour. A partial reduction of the ferric oxide to the magnetic oxide occurs [L 19]. After cleaning off the adhering loose oxide, the cycle of processes is repeated until the desired color and thickness of oxide coating are obtained, after which the surface is rubbed with oil. It is evident that the results will be largely dependent upon the skill of the workmen and that the process is a rather expensive one on account of the repeated handling necessary.

Electrolytic Process of Oxidation.

Surface oxidation of many metals can readily be accomplished by electrolytic means. Such methods are generally referred to as "anodic processes" since the metal while being treated functions as the anode of the electrolytic cell used. De Meritens [L 33], many years ago (1886), reported that he had produced an oxide coating on iron and steel by using it as the anode in a cell with distilled water as electrolyte. He reported that an adherent black finish could be obtained with a very low current density, whereas ordinarily under such conditions of electrolysis the surface was covered with a pulverulent layer of the red oxide. Recently [L 35, L 38, L 42], the anodic oxidation of iron as well as of copper and brass in a strong alkaline solution has been described and very good results claimed. Sodium hydroxide, said to contain sodium ferrite (Na_2FeO_2) in solution, is used as the electrolyte. The ferrite is produced in the caustic soda solution by a preliminary electrolytic treatment with an iron anode, a high current density being used. Any ferrate formed can be reduced to ferrite by boiling the solution with iron. The process is claimed to be applicable to cast and malleable iron as well as to wrought iron and steel. Some of the alloy steels, such as those of chromium and tungsten, oxidize with a brownish-black surface instead of black with such a treatment.

The article to be treated is first made the cathode of the cell in order to clean the surface, any rust present is removed and some reduced to iron, the current is then reversed and a dull black coating of oxide forms on the surface of the article, now the anode of the cell. A very adherent hard coating of oxide having a dull black appearance is produced.

The production of a black coating on iron electrolytically without the aid of any applied electromotive force [L 38] has been described. The iron to be treated is immersed in a sodium hydroxide solution of lead plumbite, Na_2PbO_2, contained in a lead lined tank. The sodium plumbite is obtained by dissolving litharge, PbO, in a caustic soda solution, an excess of the alkali being used. The iron articles to be treated

are in metallic contact with the lead lining of the tank and the reaction which takes place may be considered to be the result of the electromotive force of the electrolytic cell. These electrolytic methods for the coating of iron are not used commercially to any extent, however.

The electrolytic method is of considerable and growing importance in the production of protective oxide coatings on aluminum and light aluminum alloys, such as duralumin. By this means the surface oxidation which always occurs naturally to some extent is intensified. A great deal of study has been put upon the general subject of the anodic reactions of aluminum. Skinner and Chubb [L 34] appear to have been the first to utilize this reaction in a practical way, for producing a protective coating on aluminum. Their aim was to obtain a coating of alumina thick enough to serve as an electrical insulation on wire. The wire was made the anode in a solution of borax, ammonium borate or sodium silicate, and a rather high voltage (approximately 400) applied to the cell. The best results were obtained with a sodium silicate solution. The coating varied in thickness from 0.0001 to 0.0004 inch and had good insulating properties which were not impaired, apparently, by stretching the wire as much as 30 per cent. The surface of the alumina coating was rough and very sharp.

Recently, since duralumin has come to be used rather extensively as a material for aircraft construction, anodic oxidation treatment has been proposed and used to a limited extent for producing a corrosion-resistant coating on the material. A warm chromic acid solution has been found to be an excellent electrolyte for the purpose [L 37, L 43], although other solutions such as borax have also been used apparently with success [L 39]. The oxide coating formed on aluminum by "anodic treatment" in a chromic acid solution is somewhat transparent and has a very smooth shiny surface and a pleasing gray color. No visible cracks are produced by severely bending a coated sheet specimen. No results are available to show the behavior of aluminum or duralumin coated in this manner when exposed for long periods to atmospheric corrosion. In laboratory tests, however, excellent resistance to mildly corrosive agents has been obtained. A somewhat similar coating on aluminum and aluminum-rich alloys can be obtained without electrolysis, the article being merely immersed in a hot solution. Rather complex solutions, usually containing a chromium salt and potassium dichromate, are used for the purpose. The process has only recently been proposed, and information concerning the value of the coatings produced by it as a means of protecting aluminum against atmospheric corrosion is not yet available [L 44].

If the surface is greased after the anodic oxidation treatment, the corrosion resistance is improved many fold. The amount of grease used need be only very slight. For example, 0.05 ounce per square foot of surface, applied by dipping the specimen in a solution of grease in a volatile solvent, has been found by laboratory corrosion tests sufficient to give sheet duralumin a very high resistance to corrosion. Renewal of the grease film at intervals, of course, is necessary.

The anodic oxidation method has also been investigated as a means for producing a protective coating on magnesium [L 41].

Phosphate Coatings.

Iron and steel can be given a very attractive black coating which affords a fair degree of protection against corrosion by treating it in a dilute aqueous solution of phosphoric acid which is saturated with iron phosphate. The process was originally known as "Coslettizing" [L 54, L 55] after the originator of the method and later, in this country, as Parkerizing [L 58, L 59].

Iron reacts slowly with phosphoric acid with the evolution of hydrogen and the formation of ferrous phosphate, the latter substance being soluble in phosphoric acid only to a limited extent. No entirely satisfactory explanation has been advanced to account for the deposition of the phosphate on the iron in the form of a firmly adherent coating. It is usually stated, however, that on account of the solution being saturated initially with iron phosphate or becoming saturated as a result of the reaction continuing long enough, further reaction between the phosphoric acid and the iron results in slight supersaturation so that the iron phosphate forms directly on the surface of the iron. A very adherent, though thin, coating is formed. When the iron articles, after being properly cleaned, are immersed in the bath and heated (to 212° F., 100° C. approximately) hydrogen is evolved so long as any of the iron surface is exposed. The cessation of hydrogen evolution marks the completion of the treatment and the coating must necessarily *completely* cover the surface when hydrogen evolution has entirely ceased. Three to four hours' treatment is usually necessary. In the phosphate process, as developed as "Parkerizing," manganese dioxide was added to the bath, it being claimed [L 58, L 59] that oxidation of at least some of the phosphate to the form of ferric phosphate was necessary and that the coating consisted of both the ferrous and ferric phosphates. Manganese phosphate might also be deposited. Other additions to the bath have been recommended at times, the purpose of which is not at all clear.

A phosphate coating on iron, when the material is taken from the bath and dried, has a gray matt appearance. Oiling the surface renders it black, as a result of the small amount of oil which is retained. The presence of this oil film also adds materially to the corrosion resistance of such a coating. The protection afforded by a phosphate coating is, of course, only mechanical, any break in the coating soon manifesting itself by the appearance of rust at that point.

Since the coating is very thin, the process may be applied to most articles after being machined to size without any allowance in machining being made for the subsequent coating. Since the temperature used in the treatment is not above that of the boiling point of water,

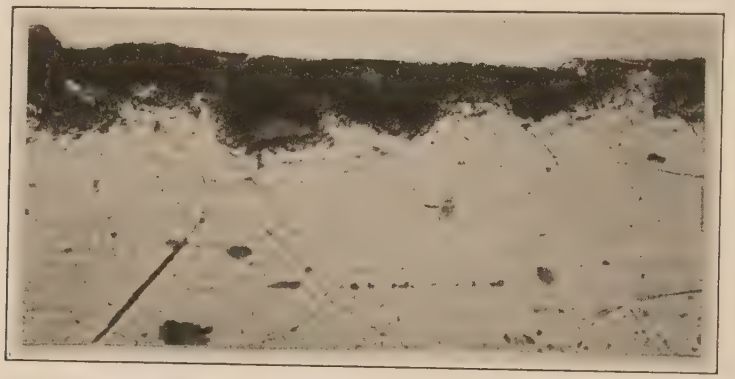

FIG. 58. Section of a soft steel sheet which has been given a phosphate coating, × 500; etched with alcoholic picric acid solution to show the grain structure of the steel sheet.

the process can be applied to hardened-steel articles, as this temperature is considerably below that used for tempering most hardened-steel pieces. Figure 58 shows a section through the phosphate-coated surface of a steel sheet.

The process is coming into rather wide use especially for small articles for which a black finish is desired and which are subjected only to mild corrosion, especially indoors. For such purposes the process is proving very satisfactory. The process should not be considered, in any way, however, as a competitor of those coating processes used for protection against severe or continued corrosion, such as all-weather out-of-doors service.

The phosphate coating is said to have very superior binding properties when used as a base for enamels and paints. Its use on magnesium as a treatment prior to enameling has been reported as a very satisfactory method for protecting magnesium against corrosion.

Miscellaneous Black Coatings.

An electrolytic method which is often used for obtaining a black finish on copper, brass, zinc, aluminum, and steel plated with any of these metals, is known as "black nickel plating" [L 60, L 61, L 62]. The solutions used as plating baths are often very complex in composition and the deposits correspondingly complex. Some of the solutions contain arsenic and the deposit in such a case consists largely of this element. Another plating solution in common use contains nickel and zinc sulfate together with sodium sulfocyanate (NaCNS). In addition to the two metals nickel and zinc the deposit contains sulfur, presumably as nickel sulfide, and the black color of the deposit may be attributed at least in part to the presence of this substance.

A variety of shop methods are used for producing a black finish on iron and steel. Oil blackening [L 47] consists in heating the articles in a box of spent carburizing compound or even in charcoal dust for one or two hours at approximately 650° C. (1200° F.), after which they are quenched in oil. A dull black oxide skin is formed in this manner.

A modified black finish having somewhat the appearance of bronze can be produced on steel by first giving it a thin coating of copper, after which the surface is blackened by immersion in a sulfide solution, such as potassium sulfide. The bronze appearance is then produced by rubbing off the black sulfide film here and there so as to reveal the copper beneath. The surface after drying is lacquered. Such coatings are used considerably, but for ornamental purposes only, the protection afforded being very slight.

Special Applications of Cementation.

Silicon Coatings.

By cementing steel or iron with silicon, attempts have been made to produce a coating highly resistant to acid. Vawter [L 63] tried to obtain such a coating by heating iron in an atmosphere of silicon hydride (SiH_4) at 400° to 600° C. (750°-1110° F.) but only a thin fragile shell formed upon the iron. By the cementation method more encouraging results have been obtained. The work of Fry [L 64] showed that a ferrosilicon of low silicon content, 21 per cent, was not suitable. By cementation of iron with a ferrosilicon containing 75 per cent silicon, at 800°-1200° C. (1470°-2195° F.), Haslam and Carlsmith [L 65] obtained coatings approximately 0.02 inch in thickness. Guillet [L 66] concluded that the addition of a small amount of ammonium chloride to the cementing mixture (ferrosilicon of 75 to 80% Si) was very advantageous, as is shown in Table 18.

TABLE 18.—CEMENTATION OF IRON BY SILICON [L 66].

"Cement" Used	Additions		Temperature	Period	Penetration: Thickness of Coating	
	NH_4Cl	SiO_2				
	Per Cent	Per Cent	° C.	Hours	Mm.	In.
Ferrosilicon 80% Si..	5	0	1200	6.45	to center of rod (1 cm. diam.)	
" " " ..	5	0	1150	3	2.5	0.1
" " " ..	5	50	1200	3	0.5	.02
Ferrosilicon 75% Si..	0	0	1100	4	0	0
" " " ..	2	0	1100	4	0.6	.024
" " " ..	0	50	1100	4	0	0
" " " ..	2	50	1100	4	1.1	.044

In all cases, the coating though uniform was very fragile, although it might be possible to improve it by proper heat treatment. A good deal of experimental work is still necessary, however, to decide definitely whether coatings of silicon are commercially feasible.

PRODUCTION OF HARDENED SURFACE LAYERS ON STEEL.

A hard surface layer on steel or any metal, produced for the purpose of increasing the resistance of the material to abrasion, may be considered as a special type of protective coating. The carburization of steel together with the subsequent heat treatment for producing the hardened condition at the surface of the steel article is of very great industrial importance. This subject of carburization will not be discussed here but reference made only to the attempts to duplicate the result in other ways.

Iron reacts readily with nitrogen under suitable conditions, giving rise to a hard constituent usually referred to as iron nitride. This reaction forms the basis of a recent process for case-hardening steel which involves no heat treatment of the article after the chemical treatment. The heating of steel in a bath of fused potassium cyanide, followed by quenching, has long been used industrially as a method of case-hardening. It has been shown recently [L 73, L 75] that the hardness of a layer produced in this manner is primarily the result of the nitrogen taken up by the steel rather than the carbon as was formerly thought to be the case. The method of case-hardening by means of nascent nitrogen by heating steel in ammonia gas at a temperature somewhat below 600° C. has been recently described [L 77, L 78, L 79]. The method gives best results with steels containing aluminum, manganese, chromium, or molybdenum [L 79]. With plain carbon steels and pure iron, the nitrogen diffuses into the metal so readily that a hard

surface coating of nitride is not built up to any extent. For commercial success with the method, it is necessary, therefore, that there be an "inhibitor" in the steel to prevent the rapid diffusion of the nitriding gas. This is the purpose of the aluminum or other elements listed above. Figure 59, from Guillet [L 82], shows the differences in the structure obtained by this process, according to the aluminum content of the steel.

No heat treatment for hardening is necessary for steels case-hardened with nitride, hence distortion or warping during quenching, which is the source of a good deal of trouble and expense in the ordinary case-hardening process, particularly of complex shapes, can be entirely eliminated. The surface hardness secured in this manner compares very favorably with that secured in the usual way by carburization followed by heat treatment, and case-hardening of steel by means of nitrogen is finding considerable commercial application especially in Germany.

Boron reacts with iron when the two are heated together and a few attempts have been made to utilize this reaction in the case-hardening of steel [L 70, L 71, L 72]. No practical applications have been made, however.

Coatings of Tungsten and Similar Metals.

Tungsten and molybdenum are highly resistant to a good many chemicals, and coatings of these metals would, without question, find a good many useful applications if they could be produced readily. A number of attempts have been made to produce tungsten by electrodeposition [L 67, L 68] but without success. By the cementation method some success has been attained. Laissus [L 69] has shown that by cementation with the powdered ferro alloy, at 800° to 1200° C. (1650°-2200° F.) in the presence of ammonium chloride vapor, coatings of tungsten, molybdenum, or tantalum can be produced on iron and on copper alloys. A somewhat lower temperature was used for the latter than that given above. The coating produced by cementation, of course, does not consist of the pure metal but a combination of the coating and the coated metal. The composition and properties of coatings produced in this manner have not been fully investigated and no practical applications of them have been made.

Cementation by Metallic Salts.

Peczalski [L 83, L 85] has described an unusual case of cementation of copper. The copper was heated while surrounded by the salt of an alkali or alkaline earth metal, such as chloride or oxide, at a temperature below the fusion point of either the copper or the salt.

FIG. 59. Steel case-hardened by the 'nitriding" process [L 82].

A, low carbon steel of carburizing grade when exposed to the action of hot ammonia gas absorbs nitrogen which readily diffuses throughout the steel. No well defined surface surface of nitride is built up. × 200. Etching, 4 per cent nitric acid solution.

B, steel containing 7 per cent aluminum, under the conditions of *A*, forms a *very* thin surface layer of brittle nitride, × 200. Etchant, picric acid.

C, surface nitride layer on a commercial aluminum steel, × 165; etchant, picric acid. The aluminum content is between 1 and 1.5 per cent, approximately.

The fracture of the cemented copper bar showed that the metal had been affected in some manner to an appreciable depth. The nature of the change produced has not been determined although it is undoubtedly a special case of the reaction between metals and fused salts discussed by Lorentz [L 84]. Peczalski stated that copper treated in this manner was superior to untreated copper for use in an electric arc, but aside from this no attempt has been made to apply in any practical way this method of coating by cementation.

Chapter 13.

Methods of Testing Metallic Coatings

Protective metallic coatings are generally used as a protection against corrosion for a metal which by itself is relatively easily attacked. The determination of serviceability in this respect of a metal spread out as a thin film on the surface of another of distinctly different characteristics is quite different from the usual corrosion test as applied to metals in general. The commonly used method for determining the corrosion resistance of a metal depends upon the determination of the loss of metal, expressed either in terms of mass or as the thickness of the layer removed, per unit of surface area per unit time of exposure to any prescribed corrosive condition. A method of this kind is of value for determining the thickness of a metallic coating but gives very little information concerning the nonuniformity of the thickness of the coating—the feature upon which the life of any coating is often primarily dependent.

As pointed out by Sang [B 48], the following properties are of importance in the consideration of any metallic coating: *a*, adherence of coating to the base; *b*, flexibility of coating; *c*, average thickness of coating; *d*, variations in uniformity of thickness; *e*, porosity; *f*, the resistance to wear; and *g*, resistance to chemical attack. The last two are of importance primarily in the comparison of coatings of different metals rather than in the routine testing of any particular kind of coated metal. However, the resistance to corrosive conditions approximating the service conditions to which the material is expected to be exposed forms the basis for the development of accelerated corrosion tests, as discussed later in this chapter.

On account of the commercial importance of such coatings most of the testing methods in use or which have been proposed are intended for zinc coatings, so that the discussion below will relate largely to coatings of this kind. The tests can be conveniently grouped under two headings, mechanical and chemical. Tests of the first kind are primarily for determining the adherence and ductility of the coatings; those of the second, for determining the weight of coating, that is, the

average thickness and variations in thickness. Defects such as porosity can also be determined by chemical tests.

Mechanical Tests.

Tests of this kind are used almost exclusively on sheet and wire since these materials are often fabricated into other forms subsequently to the coating operation. They are generally of the nature of a bend test.

Sheets.

Zinc-coated sheets are often tested by being bent double over a mandrel of a specified thickness, which is usually expressed in terms of the thickness of the sheet tested. In order to pass the test, the coating on the convex side of the bent sheet must show no signs of serious injury at the completion of the test. The test, even when carefully conducted, is only a rough one as is shown by the results in Figures 60 and 61. The results given were obtained in tests conducted under very carefully controlled conditions [M 35] for the purpose of obtaining information on the bending properties of zinc-coated sheets for use in specifications for the United States Government. The weight of coating for each specimen used was determined directly by stripping the test specimen after the bend test had been completed instead of using the average of the entire sheet. It will be noted that in a large number of cases sheets with a thick coating withstood bending double over the same mandrel thickness without serious injury to the coating just as well as the much more lightly coated sheets did.

It is often a matter of uncertainty as to what constitutes failure of the coating when a coated sheet is tested in this manner. In any series of tests, the results may range from minute cracks, readily visible only with a magnifying lens, at one extreme, to a pronounced flaking of the coating at the other extreme. Obviously the criterion which should be used in determining what constitutes a failure of the coating is the behavior of the bent specimen when subjected to corrosive conditions. It has been shown [M 35] by such corrosion tests that the serviceability of the coating with respect to severe corrosive conditions is not impaired unless the cracks in the bent coating are wide enough so that the sheet metal beneath is clearly exposed. Such a standard of reference was used in obtaining the results shown in Figures 60 and 61.

Bend tests of coated sheets are usually made in a simple manner by means of a vise. Stacy [M 35] has described several devices which have been used successfully for tests of this kind. In using any such device, however, care must be taken to control the speed at

which the specimens are bent, since, as is shown in Figure 62, sheets which can be bent double without causing any very material damage to the coating if the bending is done slowly enough, may flake very

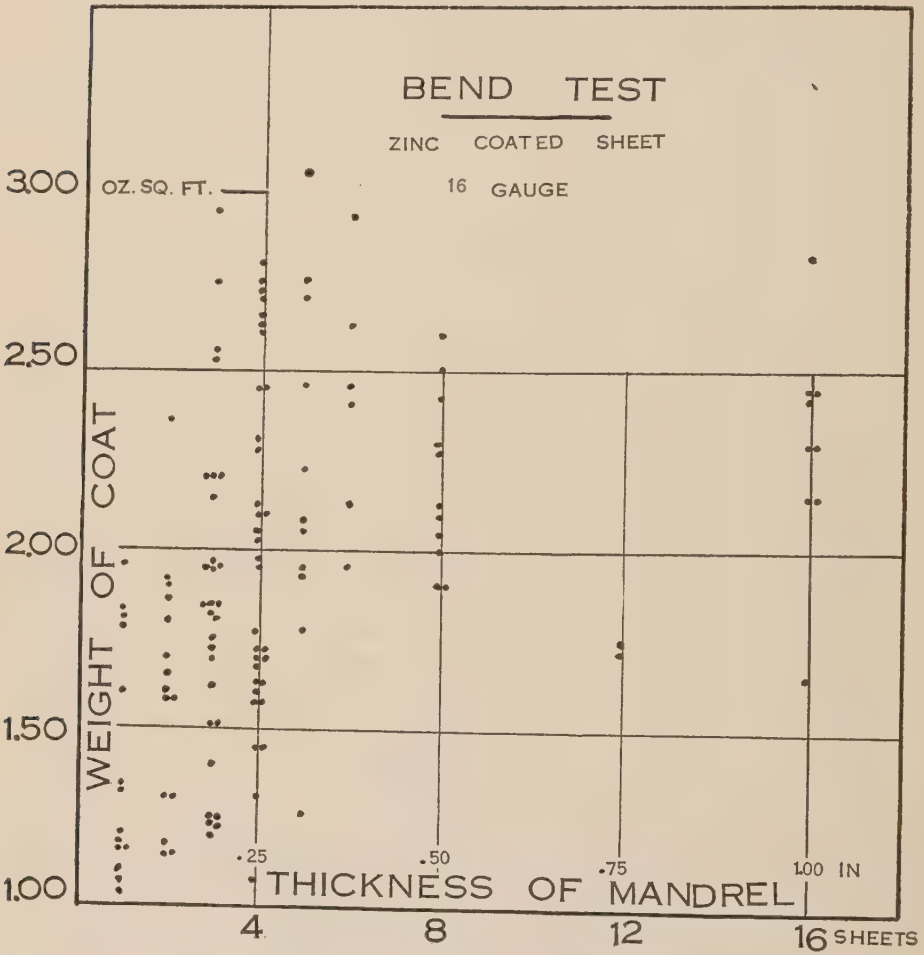

FIG. 60. Results of bend tests of galvanized sheet, 16-gage, with different weights of coating [M 35]. The tests which were all made in the same manner, a mechanical device being used. The mandrel recorded for each determination was the minimum thickness over which the sheet could be bent double without failure of the coating.

decidedly along the line of the bend if the bending is done very rapidly. This is more apt to be the case with zinc coatings having a large well developed spangle than with those having a small spangle. Experience has also shown that the temperature at which bend tests are made may

affect the results, and a minimum temperature of 65° F. (18° C.) at which bend tests may be made has been suggested for specification use [M 35].

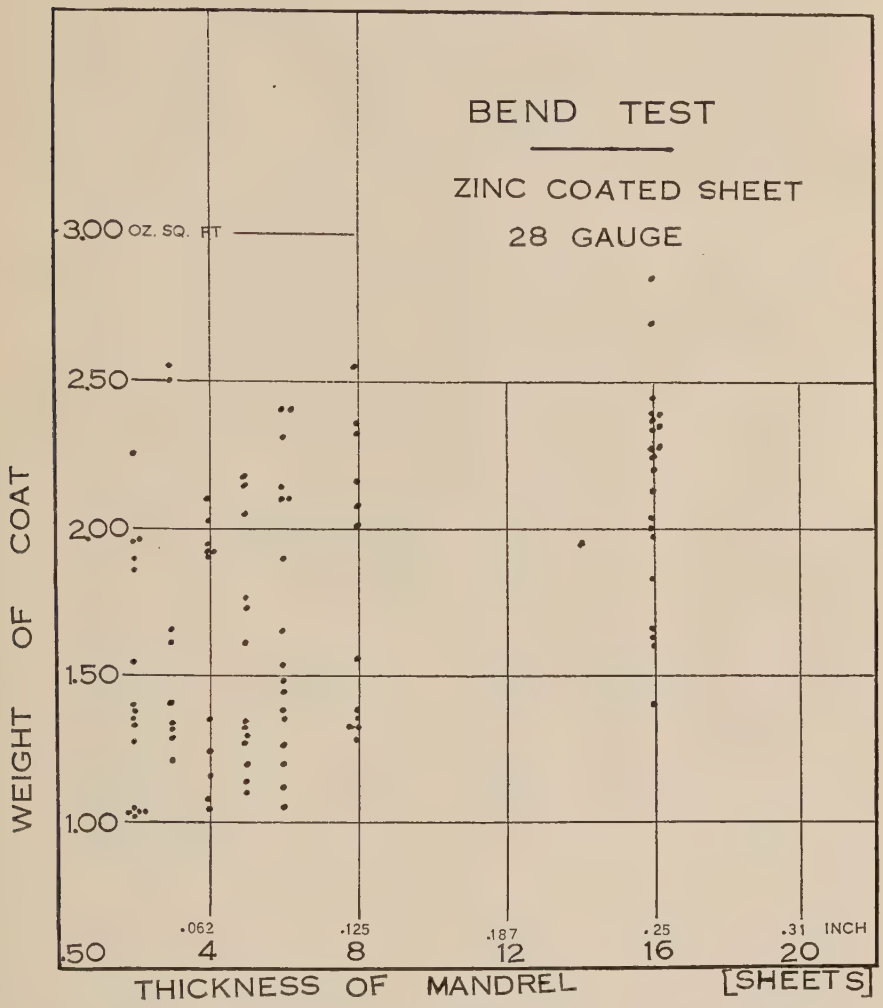

FIG. 61. Results of bend tests of galvanized sheet, 28-gage, with different weights of coating [M 35].

The bend test, aside from a practical corrugation test, in the past has not been used to any extent in American specifications for zinc-coated sheets. Recently, however, such a requirement has been introduced into specifications [B 85, B 149, M 35].

Other bend tests used for coated sheets are the 90-degree bend and "seaming" tests. They are essentially shop tests. Results obtained with the Ericksen "cupping" test on coated sheets have shown that this

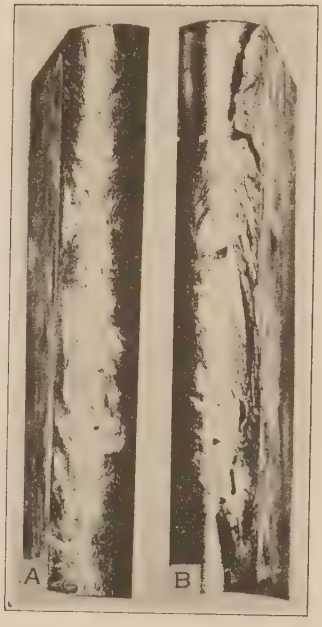

FIG. 62. Effect of speed at which the bend is made upon the results of bend tests of galvanized sheet, × 1. [M 35.]
The bends were made with a mechanical device:
A, 5 to 10 seconds required for the bending operation.
B, 1 to 2 seconds.

test is not nearly so suitable for revealing the properties of the coating as the more simple bend test is.

WIRE.

The bend test, as applied to coated wire, is carried out by wrapping the wire in the form of a close helix around a cylindrical mandrel. The coatings are graded according to the diameter of the mandrel around which the wire can be wrapped without failure of the coating [B 149]. In practice, the most severe test of this kind is to wrap the coated wire closely around a wire of the same diameter as is shown in Figure 63.

Adhesion tests.—Special tests have been proposed for measuring the adhesion of a coating to the base metal by measuring the force

FIG. 63. Representative bend tests of galvanized wires, No. 12 gage [B 121].

The bending properties of the wire are evidently influenced by the composition of the base. The coating on the wires of higher carbon content (Nos. 5 and 6) show evidence of better adherence than on the other wires.

Wire	Weight of coating	Composition of base	
		C	Mn
	oz/sq. ft.	Per cent	Per cent
1	1.1	.03	.11
2	1.06	.12	.30
3	1.13	.06	.18
4	1.55	.08	.35
5	1.20	.35	.60
6	1.08	.55	.95

A, section of the coating of wire No. 1 before and after bending, × 350.
B, section of the coating of wire No. 6 before and after bending, × 350.

A smooth alloy layer as in *B* is usually found to be associated with greater freedom from flaking than is an alloy layer with a rough irregular surface as in *A*.

necessary to tear the coating loose [B 3, E 36]. Such tests are not suitable for the routine testing of coated metals.

Chemical Tests.

Most of the tests of this kind are of the nature of "stripping tests" and may be either (*a*) qualitative, for revealing variations in thickness of coating of a single specimen or for the comparison of thickness of coating of several specimens of the same kind, or (*b*) quantitative, for determining the amount of metal used in the coating per unit area of surface covered. For coated sheets, it is the common commercial practice to express the weight of coating in terms of a unit of *sheet* rather than a unit of *surface*. A sheet bearing a 2-ounce zinc coating has 2 ounces of coating for each square foot of sheet, that is, one ounce per square foot on each side. In other cases, such as pipe and wire, the coating is expressed in terms of a unit area of surface.

Qualitative Stripping Tests.

Tests of this kind are often referred to as "field" or "shop" tests.

Preece test.—The oldest and best known test for zinc coatings is the "Preece" test, which consists in the gradual removal of the coating by repeated immersions in copper sulfate solution, the principle upon which the test is based being the displacement of copper ions from solutions of copper by ions of zinc when the latter metal is immersed in the copper solution. It has been stated [B 48] that this method of testing zinc-coated wire was used as early as 1848. Dr. Max Pettenkofer proposed this test to the Bavarian Railway Commission for comparing the zinc coatings on telegraph wires from different sources. He suggested a 10-second immersion period in a copper sulfate solution of 1 part in 12 parts of water. English wire was found to withstand 26 such immersions, whereas the Bavarian wire failed in 16. Later, the test was used in England and the name by which it is generally known now is that of Sir William Preece who strongly advocated (1884) its use for testing wire for the English telegraph lines. The test is still widely used today for zinc-coated wire.

The American Society for Testing Materials in its standard methods of determining the weight of coating on zinc-coated articles [M 28], has listed this test as a suitable field test for zinc-coated materials, and prescribes the following method for carrying it out: "The samples for the Preece test may be of any size, but should be free from as much cut surface as possible, and should be carefully cleaned before starting the test. The samples are then dipped into not less than 100 cc. of copper sulfate solution maintained at a temperature of 18° C. The samples

are allowed to remain exactly one minute in the solution. They are then washed in running water and the copper deposit lightly rubbed off. Successive immersions of one minute each are continued, with the washing and cleaning of the sample following each one until the appearance of bright adherent copper indicates that the iron beneath the coating has been exposed. Should a small amount of copper be coated adherently to the zinc coating, it must not be mistaken for the end point in which the copper plates out onto the iron. The appearance of copper within one inch of a cut surface is likewise not considered to be the end point of the test.

"The copper sulfate solution is prepared by dissolving 36 parts of commercial copper sulfate in 100 parts of water, then adding enough cupric oxide to neutralize any free acid. The solution is filtered or allowed to settle and decanted, then diluted with water until its specific gravity is 1.186 at 18° C. It should always be used at this temperature.

"When material is tested by the Preece or copper sulfate method, the number of one-minute immersions is specified.

"The amount of coating removed by a one-minute immersion in the copper sulfate solution is roughly between 0.20 and 0.25 oz. per sq. ft. of actual surface, or double this in the case of sheets".

Through a lack of appreciation of the principle upon which this test is based, and particularly as a result of the endeavor to use it in the comparison of zinc coatings differing very materially in composition and structure and hence in their reaction to the copper sulfate solution, the test has met with disfavor with many. It is a matter of rather common experience in the testing of zinc coatings that the results obtained with the copper sulfate test vary according to type of zinc coating tested. Walker [M 3] early pointed out that sherardized coatings do not give results comparable with those for other zinc coatings even of the same thickness. As previously shown (Fig. 24) the electrolytic solution potential or the "solution pressure" of any of the zinc-iron alloys is materially less than that of pure zinc. Hence it might be predicted that the rate at which such alloys will dissolve in copper sulfate or many other solutions will be noticeably slower than that of zinc. A coating with a high alloy content will withstand several more one-minute immersions in a copper sulfate solution than a pure zinc coating of the same thickness. This is demonstrated very strikingly by the following results by Peirce [M 24] which show that the rate at which the alloy layer in a zinc coating dissolves in a copper sulfate solution such as is used for the Preece test is approximately only two-thirds that of zinc in the same solution.

TABLE 19.—RESULTS OF THE COPPER SULFATE-IMMERSION TEST ON DIFFERENT TYPES OF ZINC COATINGS [M 24].

	Loss of Weight (Oz./Sq. Ft. of Surface) in Successive 1-Minute Immersions					
	1 Pure Zinc Wire	2 "Tight Wiped" Galv. Wire No. 9 [a]	3 "Tight Wiped" Galv. Wire, No. 12 [a]	4 Com'l Heat-treated Galv. Wire, No. 12 [a]	5 Unwiped Galv. Wire, No. 12 [b]	6 Same as 5, Heat Treated [c]
Dip No. 1.....	0.093	0.090	0.091	0.117	0.137	0.132
" " 2.....	.152	.097	.118	.108	.180	.131
" " 3.....	.165	.103	.110	.092	.178	.128
" " 4.....	.159	.108	.091	.096	.175	.113
" " 5.....	.159	.095	...	.103	.157	.099
" " 6.....	.165	.084	...	.102	.132	.078
" " 7.....	.155	...	...	...	...	.063
" " 8.....	.157	...	...	...	...	.045
Aver. loss per dip.	.151	.101	.103	.109	.169	.105
Aver. no. of dips for "failure" ...	...	5.7	4.	5.7	5.7	7.5
Initial weight of coating by stripping	...	.64	.458	.683	1.109	.885

[a] Microscopic examination showed the coating to be nearly all alloy.
[b] Only a thin alloy layer was found in the microstructure.
[c] Wire No. 6 was heated 1½ hours at 350°C., the total weight of coating was decreased somewhat; in structure it was almost entirely alloy.

Other solutions, such as ferrous sulfate, have been suggested for use in place of copper sulfate in a stripping test for zinc coatings [B 48]. Nothing has come of such suggestions, however. The objections which have been raised are against the test and not against the use of any particular solution.

The initial character of the surface of a zinc coating may sometimes affect, very materially, the results of the copper sulfate test. Results obtained at the Bureau of Standards have shown that zinc coatings which had become covered with a white film of zinc oxide (or hydroxide), when cleaned in the ordinary manner before applying the Preece test, at times showed an adherent film of copper at the end of the first or second one-minute immersion of substantially the same appearance as that which ordinarily indicates the conclusion of the test. However, if the filmed coating were cleaned by a preliminary momentary dip in dilute hydrochloric acid, it was found that the coating would withstand as high as 8 immersions in the copper sulfate solution before evidence of failure was obtained.

So long as the copper sulfate test is restricted to the comparison of materials which have been coated in the same manner, very useful in-

formation on the relative thickness of such coatings and the variations in thickness in the coating of individual specimens can be obtained. It should not be claimed, however, that, since zinc coatings of a high alloy content show a greater resistance to the corrosive action of a copper sulfate solution than do coatings of purer zinc, they will also resist atmospheric corrosion better. An atmospheric corrosive attack is the result of the combined effects of a number of factors, both of corrosion and erosion, and the information as to the relative resistance of different types of zinc coatings, such as can best be obtained from out-of-doors exposure tests extended over a considerable number of years, is not yet available [M 37].

Acetic acid-hydrogen peroxide immersion test.—A method described by Wernlund [M 30] and recommended by him for zinc coatings produced by electroplating consists in the immersion of the specimen in a mixture of dilute acetic acid and hydrogen peroxide. A solution of 140 cc. of 3 per cent hydrogen peroxide solution and 20 gm. of acetic acid in one liter of water was recommended, the test to be carried out at 95° C. The test is applicable only to zinc-plated ferrous materials. The time in seconds required for the appearance of red rust-spots is to be noted. It is stated that the method is useful for showing the relative value of different zinc-plating processes, especially in baths of different compositions. No data are available as to the use of the test on other types of zinc coatings. It would seem, however, that it would not be suited to those coatings containing a considerable amount of iron.

Sulfurous acid immersion test.—Immersion in sulfurous acid (approximately 6% solution) has been recommended by Pfann [M 7] as a simple means for distinguishing between zinc coatings produced by hot-dipping and by electroplating. With coatings of the first class a pronounced evolution of gas results upon immersion in sulfurous acid but not with those in the electroplating zinc coatings.

Hydrogen-evolution method.—Another field test for zinc coatings listed by the American Society for Testing Materials [M 28] is the hydrogen-evolution method. The amount of hydrogen evolved when a zinc coating is treated with dilute hydrochloric acid forms the basis of the method as described by Cushman [M 18], and is intended primarily for coated sheet material. This method which is an adaptation and improvement of an earlier one referred to by Walker [M 3] does not necessitate the mutilation of the material by cutting out small specimens. A circular ring is sealed onto the surface to be tested in such a manner as to expose an area of known size, usually of 2½-inch diameter, and the apparatus which is to be filled with dilute acid is attached to the

ring. The hydrogen evolved from the action of the acid on the coating is collected in a suitable gas burette and the amount of zinc corresponding to any volume can easily be computed. A small amount of antimony chloride is added to the acid, as described below in order to prevent any attack of the base metal.

It has been stated [M 28] that the results obtained check very closely with those obtained in the quantitative stripping method as carried out in the laboratory in which the same reagents are used. The number of occasions when a test of this character must be applied is quite limited, however. The method is used to some extent in the laboratory for the routine determination of the zinc coating on small articles. After the preliminary calibration of the apparatus, the determination of the total weight of coating can be made in a few minutes.

Heat-of-reaction test.—A method described by Strickland [M 20] for the evaluation of the weight of a zinc coating is based upon the heat of reaction between the zinc and the acid used to dissolve it. The method is especially applicable to sheet and wire. The volume of solution as well as the mass of the specimen immersed must be controlled. The maximum rise of temperature attained by the solution is noted and the weight of coating calculated by means of a formula derived empirically by using a series of weighed and measured specimens of zinc-coated material of the same kind as the unknown material to be tested. The advantage claimed for the method, that of rendering the use of an analytical balance unnecessary, does not weigh very heavily in favor of the test, however.

Gelatin test for porosity of coatings.—The test used for revealing discontinuities such as pinholes in the tin coating on tin-plate is usually credited to Walker [M 2]. This porosity test is especially useful for coatings which protect the base metal in a mechanical way only. The usefulness of any such coating necessarily depends on its impervious ness; at any perforation the corrosive attack of the base metal, as a general rule, is accelerated by the "cathodic" coating. A solution of agar in hot water to which a small amount of potassium ferricyanide and hydrochloric acid or sodium chloride has been added, is poured over the clean surface of the sheet of tin plate to be tested, which is then allowed to stand for several hours, until the gelatin has solidified. Ferrous chloride formed by the action of the acid upon any exposed iron of the base metal reacts with the potassium ferricyanide to give a blue precipitate, Turnbull's blue, and thus marks (in the solidified gelatin film) the location of the pinholes in the coating. The solution for this test, sometimes referred to as the "ferroxyl" test, may be prepared as follows: agar 1.0 gm., sodium chloride 10 gm., potassium

ferricyanide 1 gm., and water sufficient to make 1 liter of solution. A few drops of phenolphthalein are added to the solution.

The number and size of such spots vary considerably in different grades of tin plate as shown in Figure 64. It has been questioned, however, whether each blue spot produced by this test necessarily indicates an opening in the tin coating, as the crystals of the iron-tin compound in the coating which result from the alloying action of molten

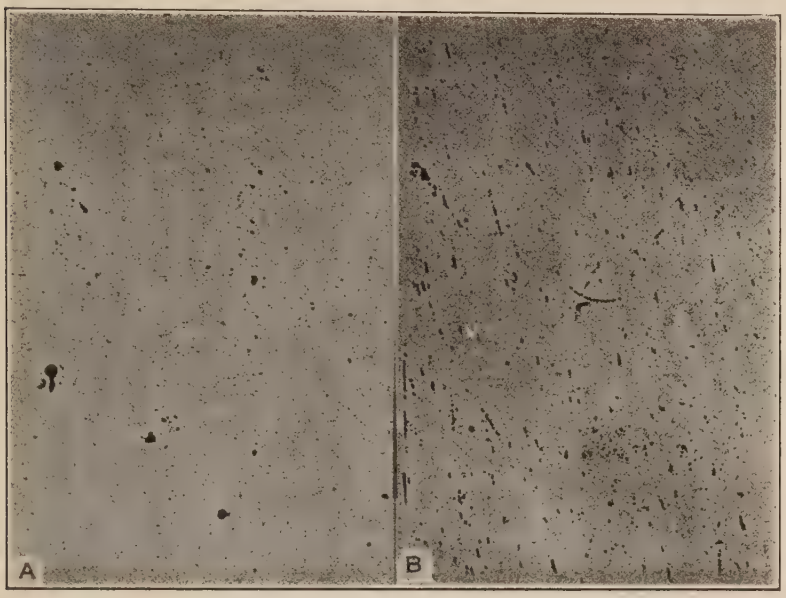

FIG. 64. Results of "gelatin test" on tin-plate [C 59].

A, commercial charcoal plate.
B, commercial coke plate.
Each dark spot appears as a blue caloration in the gelatin film and marks the location of a "pin hole" perforation in the coating, or perhaps in a few cases a crystal of iron-tin compound, $FeSn_2$.

tin on the iron in the hot-dipping process will produce the same result, and thus erroneous conclusions as to the number of pinholes may be drawn [C 59].

The gelatin test, in slightly modified form, has been used with success in the study of the relative porosity of electroplated nickel coatings made under different conditions of deposition [E 31], and recently [M 41] the method has been much simplified for use with metallic coatings, the gelatin layer being replaced by paper impregnated with the substances usually added to the gelatin in the older form of the test. The treated paper, after being moistened, is held in contact with the

coating which is to be tested for porosity. Very promising results have been claimed for the test in this form for nickel and chromium coatings.

Walker [M 3] proposed the use of a boiling solution of sodium hydroxide for revealing the pinholes in zinc coatings. The location of any discontinuities in the coating by which the iron base is exposed is shown by a stream of tiny bubbles of hydrogen at such points. It does not appear, however, that the test has been used to any extent, at least commercially, as the presence of pinholes in zinc coatings is not the cause for concern that it may be in other kinds of coatings.

Quantitative Methods; Determination of Weight of Zinc Coatings.

Although these methods are termed quantitative, they are so, only in that the weight of coating is determined rather accurately. No attempt is made, as a rule, to determine quantitatively the composition of the coating. The methods discussed below relate to zinc coatings. When it is necessary to determine the weight of such coatings as silver or nickel the coating is removed by suitable electrolytic means from a measured area and the weight per unit area determined from the loss of weight upon stripping [M 39]. Zinc coatings can be readily stripped from the base without resorting to electrolysis.

Shop weighing.—This is for the purpose of determining the average weight of coating of sheets. The recommendations of the American Society for Testing Materials [M 28] are as follows:

"Select a pickled and washed sheet. Stand the sheet on edge and allow to drain for 2 minutes. The water remaining on the sheet will then amount to approximately 0.01 lb. per sq. ft.

"Weigh this sheet with an accuracy of 0.05 lb., and subtract the weight of the water to obtain the real weight of the uncoated sheet. After galvanizing, reweigh the sheet. The increase in weight represents the coating.

"Where greater accuracy is desired, wash, dry and weigh 10 sheets; then coat and reweigh."

Sampling.—The laboratory determination of the weight of coating on zinc-coated sheets is almost always carried out on square specimens, 2¼ by 2¼-inch, the advantage of using this size is the fact that the weight of the coating in grams is numerically equal to the weight as expressed in ounces per square foot. In sampling sheets, the American Society for Testing Materials has recommended that a strip 2½-inch wide be cut transversely or diagonally across the middle of the sheet with its ends approximately one inch from the edge of the

TABLE 20.—SAMPLING OF ZINC-COATED WIRE[1] [M 28].

Birmingham Wire Gage	Size of Wire	Length of Wire for Test	
	Diam. Inch	Inch	Cm.
0	0.340	4¾	12.1
1	.300	5⅝	13.7
2	.284	5 11/16	14.5
3	.259	6¼	15.9
4	.238	6 13/16	17.3
5	.220	7⅜	18.7
6	.203	7 15/16	20.2
7	.180	9	22.8
8	.165	9 13/16	24.9
9	.148	10 15/16	27.7
10	.134	12 1/16	30.6
11	.120	13½	34.2
12	.109	14 13/16	37.7
13	.095	17	43.2
14	.083	19½	49.5
15	.072	22 7/16	57.0
16	.065	24⅞	63.2
17	.058	27⅞	70.8
18	.049	33	83.8

[1] The weight of coating in grams for the specimen is numerically equal to the weight of coating for the wire expressed in ounces per square foot.

sheet and that three specimens, cut accurately to size 2¼ by 2¼-inch be used, one from the middle and one from each end of the strip.

In sampling wires, 12-inch lengths are convenient specimens to use. It is more convenient in routine work to use such a length that the weight of coating in grams as determined in a stripping test will equal numerically the weight of coating as expressed in ounces per square foot of surface. Both the diameter and length of specimen must be taken into consideration. Table 20 gives the length to be used for wires of different diameters.

For pipes, it is frequently desirable to determine separately the weight of coating of the outside and the inside surfaces. For miscellaneous hardware, a definite sampling procedure is not practicable on account of the diversified nature of such products. For small pieces, the entire article is used and in the case of nails, bolts, nuts, rivets and other fasteners, several of the articles are combined as one sample, the number used depending upon the size in each case. Since the cutting of samples from sheet-metal ware, ash cans, garbage cans, tanks, laundry tubs and the like, as well as culverts, is not desirable, the "spot" test (p. 219) may often be found the most satisfactory method of testing such materials.

Hydrochloric acid-antimony chloride method.—This method which was first described by Aupperle [M 11] has been designated as

standard by the American Society for Testing Materials. It consists in the removal of the zinc coating from an accurately measured and weighed sample by immersion in concentrated hydrochloric acid (sp. gr. 1.19) to which has been added 5 cc. of antimony chloride solution to each 100 cc. of acid. The antimony chloride prepared by dissolving 20 gm. of antimony trioxide or 32 gm. antimony trichloride in one liter of concentrated hydrochloric acid is for the purpose of inhibiting the attack of the acid on the base metal when the coating has been removed, and unless the test specimen is allowed to remain in the acid for several minutes after the evolution of hydrogen ceases, the attack is entirely negligible so far as the accuracy of results of this test for commercial purposes is concerned [M 15]. For testing sheets, the recommended method [M 28] is as follows: "Cut three 2¼ by 2¼-inch laboratory samples as described under 'sampling' and weigh together after cleaning and drying. (If it is of interest to know the individual weight of coating on each piece, each must be analyzed individually instead of collectively as described.) They should be immersed singly in 100 cc. of hydrochloric acid (sp. gr. 1.19) to which has been added 5 cc. of antimony chloride solution, and allowed to remain therein until the evolution of hydrogen has ceased or until only a few bubbles are being evolved. This requires about 15 to 30 seconds, except in the case of sherardized coatings which require a somewhat longer time. The same 100 cc. of hydrochloric acid can be used for at least 5 samples, but 5 cc. of the antimony chloride solution should be added before the immersion of each sample. After stripping, the samples should be washed and scrubbed under running water, dried with a towel and laid in a warm place for a short time. The samples should be again weighed together and the number of grams lost divided by the number of samples taken. Each gram then corresponds numerically to one ounce of coating per square foot."

The method is applicable to the testing of wire, in which case a small piece of the wire should be stripped of its coating by a preliminary test, and the diameter measured on this rather than on the coated wire. If the length of wire given in Table 20 is used, the loss of weight in grams is numerically equal to the weight of coating expressed in ounces per square foot of actual surface.

Basic lead acetate method.—This method of stripping a zinc coating from its base, described by Patrick and Walker [M 5] has been recommended as an alternate method by the American Society for Testing Materials. A solution is prepared by dissolving 400 gm. of crystallized lead acetate in 1 liter of distilled water and then adding 4 gm. of finely powdered litharge (PbO). The solution is allowed

to settle and the clear portion used. The specimens, prepared as in the previous test, are immersed singly in a small glass beaker containing a sufficient amount of solution to cover the sample when in an upright position. A drinking glass with slightly sloping sides is a very suitable container for the purpose. After being immersed about 3 minutes, the sample is removed and the adhering lead brushed off under running water, care being taken not to brush so vigorously as to burnish the lead onto the surface. Four 3-minute immersions are usually sufficient for the complete removal of the coating, after which the stripped samples are treated as in the previous method.

The method of stripping a zinc coating by hydrochloric acid is to be preferred to the lead acetate method, especially on account of its simplicity and the ease and rapidity with which it can be carried out and not necessarily because of its greater accuracy. As a rule, the results of both methods agree fairly closely. In a report by Rawdon [M 15] of a study of these two test methods as applied to sheets and wire, carried out by a subcommittee of the Committee on Corrosion, American Society for Testing Materials, it was shown, however, that the results obtained by eight co-operating laboratories working independently on the same materials with the lead acetate method agreed slightly better among themselves and with the nominal or mill value obtained by weighing the sheet before and after being coated, than did the results obtained with the hydrochloric acid method for the same material. The average of the results obtained with the latter method for any given material was, in most cases, slightly higher than that for the lead acetate method. The basic lead acetate method is not to be recommended for coated articles of irregular shape, as the complete removal of the precipitated lead from crevices and re-entrant angles is not easily accomplished. The hydrochloric acid method is by far the better in such cases. The difficulty in determining the true surface area of objects of irregular shape is one which is hard to meet. In the case of zinc-coated nails, the weight of the coating is reported in per cent of the weight of the original coated nail.

Other methods.—A method recommended by Bauer [M 10] for the determination of the weight of zinc coatings produced by hot-dipping and also for distinguishing between this class of coatings and those produced by electroplating consists in the use of dilute sulfuric acid (approximately 2% by weight) containing 2 gm. of arsenic trioxide per liter, the arsenic being added for the same purpose that antimony is used in the hydrochloric acid method. Bauer concluded that any iron in the solution after dissolving the coating came from the zinc-iron alloy. If lead has been used in the galvanizing process, it shows in part as

adhering spots on the test sample and also as "flocks" in the solution. For electroplated zinc, the solution is clear, free from iron and there is no evidence of lead.

Another alternate method proposed by the American Society for Testing Materials [M 28] depends on the dissolving of the zinc coating in dilute sulfuric acid (10% by volume) followed by titration with potassium permanganate to determine the iron present.

Dilute sulfuric acid for stripping the zinc coating was used formerly more extensively than at present. Burgess [B 3] advocated its use over twenty years ago. In the other methods recommended above, the weight of coating determined takes no cognizance of the fact that considerable iron may go to make up the coating. The results obtained in all such cases should be reported as the weight of *coating* and not as the weight of *zinc*.

Accelerated Corrosion Tests.

Tests of this kind are intended for obtaining results within a relatively short time, preferably a few days or weeks, which simulate those which would ultimately occur in service. So far, such tests are chiefly valuable for what they indicate rather than for what they prove, since direct correlation of service results with those obtained by such tests has not yet been made. Some of the accelerated corrosion tests, however, give very useful information concerning the relative behavior of different types of coated metals when subjected to the same corrosive conditions.

Spray Test.

This test which was first described by Capp [M 9] and later in an improved form by Finn [M 16] is generally carried out as a "salt-spray" test. A nonmetallic covered container, preferably of glass, soapstone, earthenware or wood, is used as the chamber for the specimens which are suspended or supported so as to permit free access of the mist or cloud of the atomized solution of sodium chloride which fills the closed container. The form used by the United States Bureau of Standards is a rectangular soapstone box with a glass cover, held in an inclined position so as to form a reservoir for the solution to be sprayed by the atomizer at the lower end of the box. The specimens to be tested are in the upper part of the box. The diagram in Figure 65 is that of a longitudinal section through the box.

A 20 per cent solution of commercial sodium chloride (20 g. salt in 80 cc. water or 2 lbs. to 1 gallon) has been found suitable for use [M 19], although a much less concentrated solution is often used with

complete satisfaction. The air supplied by a small blower at approximately 10 pounds pressure should be passed through a plug of cotton wool to filter it free from oil and then be bubbled through water in order to saturate it so as to retard crystallization of the salt around the opening of the atomizer.

The test procedure is often varied. The test may be continuous, the specimens being taken out at stated intervals, for example, at the end of every 24-hour period, washed under running water and brushed

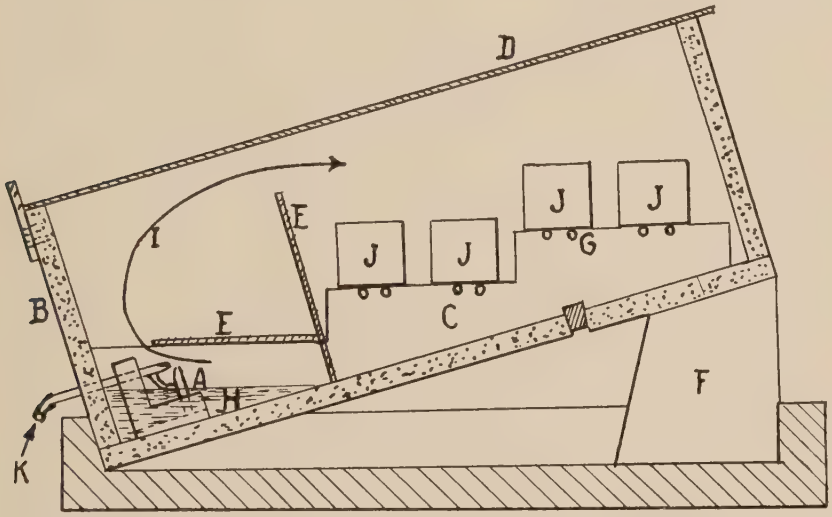

FIG. 65. Section of the "spray box" used in the "spray" corrosion test. [M 19].

A, atomizer
B, stone box
C, stone supports
D, glass top
E, glass baffle plates
F, base support
G, specimen supports
H, solution
I, path of spray
J, specimens
K, tube for compressed air

with a bristle brush and examined after drying for evidence of rust, after which they are put back into the "mist box." In some cases, the test period is broken up into cycles, each cycle comprising an exposure in the salt mist followed by a drying period in the air before the specimens are cleaned and examined. It is claimed by some that such a procedure simulates more closely the conditions obtaining in service, for example, near or along the seacoast, than does the first method. In both cases, the first definite appearance of rust of the base metal is taken as the end point of the test, although valuable evidence is often secured by continuing the test for some time after this.

Concerning the indications of the results of the salt-spray test on

zinc-coated materials with respect to the service which may be expected from such materials, the Bureau of Standards has stated [M 19] that if rust appears within 24 hours, the material is unsuited for outdoor exposure; if within 36 to 72 hours, the material may be considered

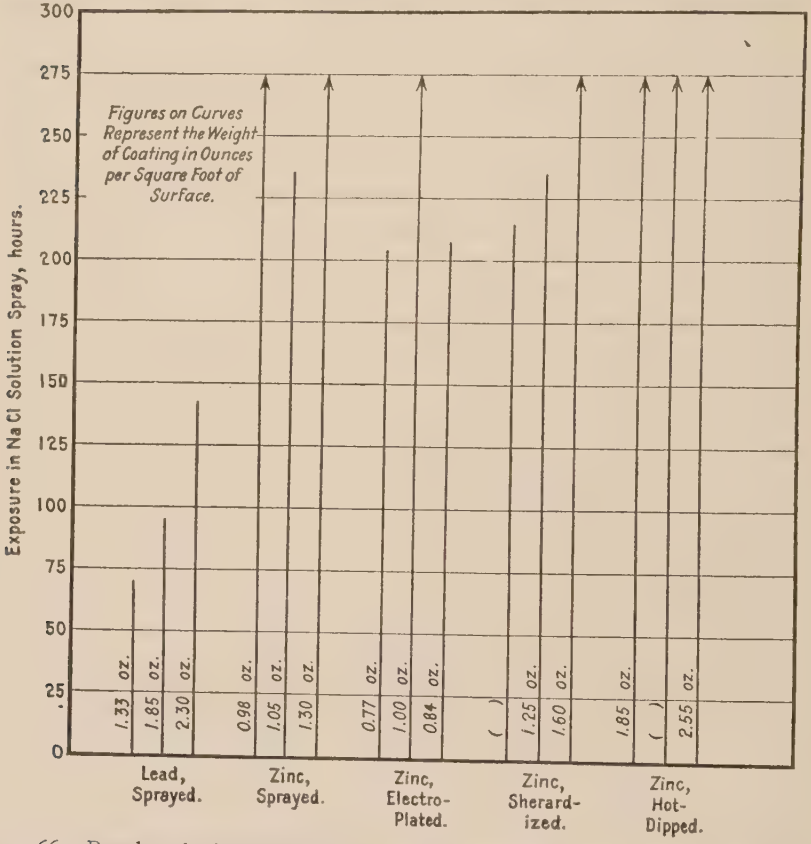

FIG. 66. Results obtained with the "spray" corrosion test on sheet steel zinc-coated by different methods [M 38].

The arrows indicate that the coating was still in good condition when the test was ended. In other cases the length of the line gives the "life" of the coating under the conditions of the test. Special material was made for the test, the weight of coating being accurately determined on each sheet by weighing before and after coating.

suitable for mild exposure, but for severe exposure, 96 to 144 hours' continuous exposure in the salt spray without any appearance whatever of rust is required. Most hot-dipped zinc coatings, with a weight of coating of three-fourths to one ounce per square foot of surface, will successfully withstand a very much longer exposure than this unless initially defective.

In Figure 66 are summarized the results obtained with this test on sheet steel coated in five different ways [M 38]. The comparison of these results with those obtained on similar material with other tests is of interest (Figs. 67 and 69).

An objection which has been raised to this method of accelerated corrosion testing for zinc-coated materials is that the conditions which obtain are at times distinctly different from actual service conditions. The rather firmly adhering deposits of basic zinc salts which may form over the surface of the zinc coating, in the course of the test, give considerable protection so that a fictitious value may be obtained for a coating which may be somewhat misleading. Under ordinary atmospheric service conditions, the corrosion film which forms on the surface of a zinc coating is of an entirely different character from the deposit of corrosion products formed in this test.

For nickel and other types of "cathodic" coatings, the spray test has been found to be a useful means for revealing porosity of the electroplated coatings. Baker [E 28] in his application of the spray test in evaluating nickel coatings, has emphasized the desirability of continuing the test considerably beyond the time of the first appearance of rust. The rate at which the rust forms after its first appearance varies very considerably for different specimens. The following method of rating nickel coatings by means of the spray test, according to Baker, has been found much more useful than a mere statement of the total number of hours' exposure required for the formation of rust.

The final rating of any coating is the sum of the individual ratings for the various corrosion periods required to give the surface a very noticeably rusted (VNR) appearance. For example, a specimen rated "P" after the first corrosion period, "SR" after the second, "NR" after the third and "VNR" after the fourth would have a final rating of 10 $(4 + 3 + 3 + 0)$. Such a rating method is evidently more suited to the case of coatings such as nickel which show rusting relatively quickly, than for heavy zinc coatings, which will withstand the corrosive action of the spray for a very much longer time. As a matter of fact, the spray test is by far much more useful for testing coatings of the former type than for the latter.

Considerable study of the spray test as a means for determining the relative corrodibility of metals has been carried out as part of the program of one of the committees of the American Society for Testing Materials [M 32]. The results of this study have served to emphasize some of the precautions which must be observed in carrying out this test. The specimens must be protected by a baffle plate from the direct impinging of the spray stream from the atomizer upon them, and their

TABLE 21.—METHOD OF RATING THE RESULTS OF THE SPRAY CORROSION TEST [E 28].

Corrosion Period No.[a]	Numerical Rating According to Degree of Rusting				
	P	VSR	SR	NR	VNR
1	4	3	2	1	0
2	5	4	3	2	0
3	6	5	4	3	0
4	7	6	5	4	0
5	8	7	6	5	0
6	9	8	7	6	0
7	10	9	8	7	0
8	11	10	9	8	0
9	12	11	10	9	0

[a] The corrosion period, which should always be the same in any series of tests, may be any convenient period, e.g., 8 or 10 hours.

P, perfect, no trace of rust seen on close scrutiny.
VSR, very slightly rusted, very close examination shows only a trace.
SR, slightly rusted, close examination shows distinct sign of rust.
NR, noticeably rusted, moderately close examination shows presence of rust.
VNR, very noticeably rusted, rust plainly discernible at a distance of 3 or 4 ft.

position within the box should be changed at regular intervals; the specimens should be supported from beneath rather than suspended from a hook, and if several kinds of metals are exposed simultaneously within the box, precautions to guard against contamination of the fresh solution by the products of corrosion should be taken, especially if the test is used with solutions which give a soluble corrosion product.

Dilute solutions of ammonium chloride have been used to some extent in the spray test for zinc coatings. The time required to cause failure of the coatings is much less than for sodium chloride and the corrosion product is not nearly so adherent.

SIMULATED ATMOSPHERIC TEST.

Zinc is very appreciably corroded by atmospheric agencies, the chief ones being sulfurous acid and carbonic acid. A test for zinc coatings based upon this fact was used by Szirmay [M 1] over twenty years ago. The specimens were suspended under a glass bell jar and air containing 12 per cent of sulfur dioxide and 15 per cent of carbon dioxide was passed into the bell jar. An open dish of water under the jar permitted saturation of the air at the temperatures used which were varied between 6° and 45° C. The test was used primarily to determine relative resistance of zinc coatings produced by hot-dipping and by electroplating. Heyn and Bauer [M 6] later made use of this test in studying the relative resistance to corrosion of various zinc-coated pipes.

Finkeldey has described [M 23] a very much improved form of test

of this kind. As carried out on a scale sufficient for a manufacturing plant, a lead-lined wooden tank approximately 70 by 40 by 45 inches high constructed of cypress lumber 2 inches thick was found very satisfactory. The cover, which is also lead-lined, is fitted in such a manner into a trough containing water so as to make a water-seal. The tank is filled to a height of 6 inches with water, the latter being heated electrically to a temperature sufficient to give an atmospheric temperature of 55° C. in the proximity of the specimens which are supported on a false bottom just above the surface of the water. A gas mixture consisting of 100 volumes of air, 5 volumes of carbon dioxide, and 1 volume of sulfur dioxide, these volumes being controlled by a suitable flowmeter, is admitted from a mixing chamber to the tank at one end just above the water level and by means of the false bottom is made to traverse the length of the tank over the surface of the water before coming in contact with the specimens. The gas is allowed to flow at the approximate rate of 6.4 liters per minute, the exhaust being large enough to prevent the pressure from building up within the tank.

The test is carried out in cycles, each cycle consisting of (*a*) an exposure of the specimen to the warm moist corrosive atmosphere for 10 hours, (*b*) thorough washing with a heavy spray of water for 2 hours, and (*c*) drying in ordinary atmosphere at room temperature for 12 hours. The number of cycles required to produce perceptible rusting of the steel or iron base of the zinc-coated material is taken as a measure of the relative corrosion resistance of the various materials tested. The coatings are examined for failure during the drying period. All cut edges of the specimens are protected in order to prevent rust stains from this source on the surface of the specimen under observation.

As yet no recommendations have been published as to the relation between the kind of service for which a zinc-coated material is suited and its behavior when tested in this manner. As pointed out by Finkeldey [M 23, *discuss.*] the appearance of the surface of zinc-coated sheets taken out at intervals during the progress of the test very closely resembles the appearance of similar zinc-coated sheets after various lengths of time in ordinary service, that is, as subjected to atmospheric corrosion. After one or two test cycles the bright spangled appearance becomes much subdued and the sheets lose their metallic luster and show a light gray film. The spangles gradually disappear after additional cycles and finally dark spots, which appear black when covered with a film of water, show here and there over the surface, often along the margin of the spangles. They are the result of the uncovering of the zinc-iron alloy layer. As the test proceeds the entire surface becomes dark on account of the complete removal of the outer zinc-

rich layer and the exposure of alloy layer. Finally, rust spots appear as the steel or iron base is exposed. During the course of the test, the specimens, after the exposure to the corrosive atmosphere, often show a red or yellowish film of rust which results from the attack of iron of the alloy layer and is readily distinguishable from the rust

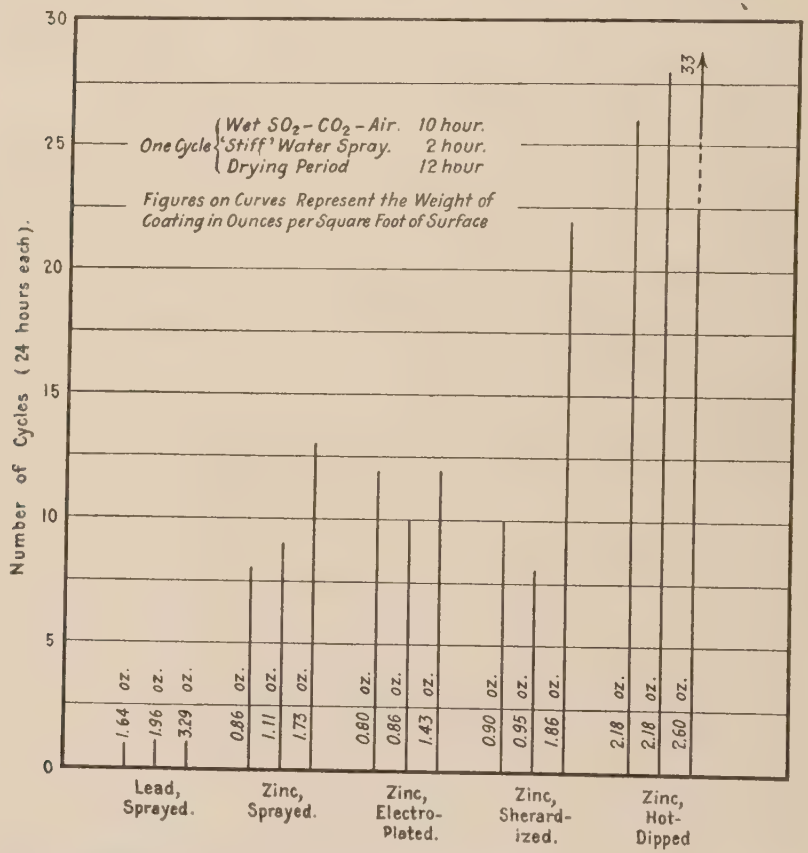

FIG. 67. Results obtained in a simulated atmospheric test on zinc coated sheet steel [M 38]. The material was similar to that of Fig. 66.

which forms on the base metal when the coating has been corroded through.

By a very gradual stripping test of this kind, it is possible to estimate rather closely the relative life of the outer or zinc-rich layer and of the underlying alloy which often constitutes the greater part of a hot-dipped zinc coating. This is a point upon which very little information is available.

In Figure 67 are given the results obtained with this test when applied to the coated materials of different kinds made for the tests and for which the weight of coating was accurately known.

Fowle [M 31] has described a very similar accelerated large-scale corrosion test for the testing of wire. In this, bituminous coal smoke was used instead of the corrosive gas mixture given above.

Intermittent Immersion.

The intermittent immersion method [M 22, M 23, M 25] has been used to some extent as an accelerated corrosion test method for coated metals. This test may be carried out as a series of immersions repeated

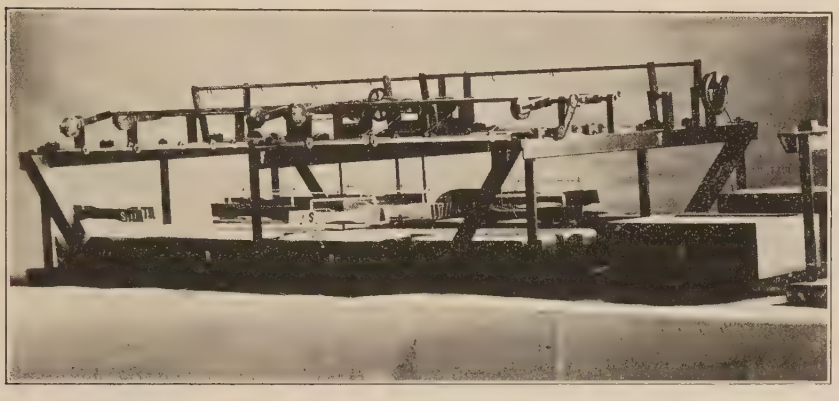

Fig. 68. Form of apparatus used for the intermittent-immersion corrosion test [M 23].

The specimens *S* are dipped into the solution in the containers *R* as the cranks *C* are rotated at intervals controlled by the clock *B* through the device *T*.

indefinitely at short intervals or intermittently. In the second case, the interval between two successive immersions is usually made sufficiently long so as to permit drying of the surface of the specimen.

Figure 68 shows one form of apparatus used for conducting this test. The specimens are hung on horizontal rods which are raised and lowered by means of crank-arms at the ends. The motor which rotates the cranks is controlled by means of suitable timing device so that it is started at chosen intervals and allowed to operate long enough to permit the specimens to be lowered into the solution and then withdrawn into the air.

A simpler form of apparatus consists of a light wheel mounted so as to rotate about a horizontal axis. The specimens are attached along its periphery in "Ferris Wheel" fashion and as the wheel rotates the specimen on at lowest point of the wheel is drawn through a shallow

tank containing the corroding solution [M 25, *discuss.*]. The test, as carried out in this manner, has been applied by Thomas and Blum [E 31] in the determination of the relative porosity of nickel coatings.

Farnsworth and Hocker [M 22] have described the use of the intermittent immersion method for the evaluation of zinc coatings. They

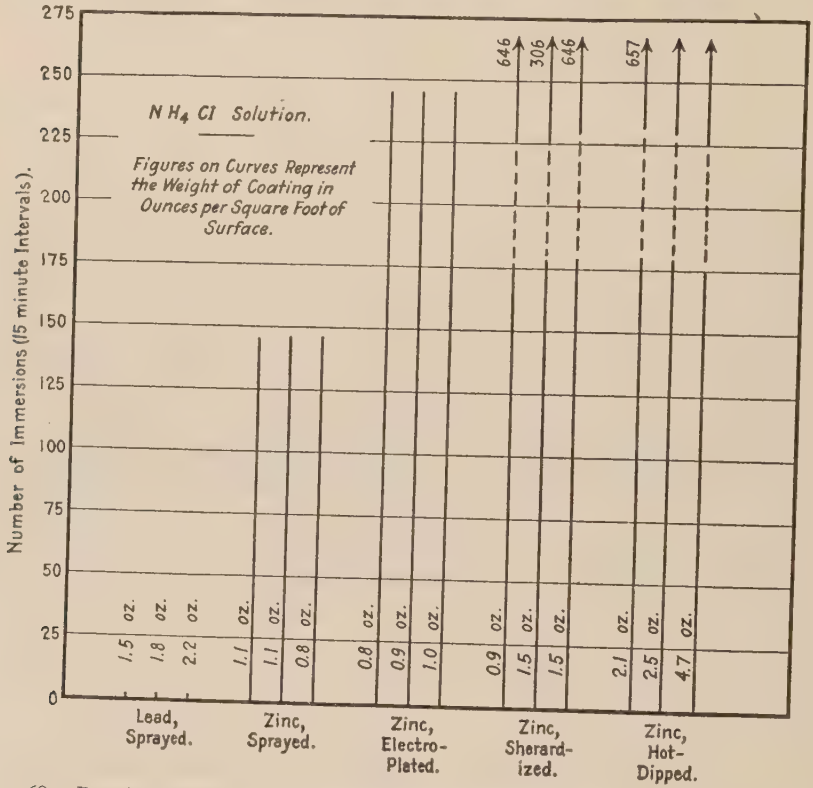

FIG. 69. Results obtained by an intermittent-immersion corrosion test on zinc-coated sheets [M 38].

The material was similar to that of Fig. 66. The arrows indicate that rusting of the steel base had not yet occurred when the test was ended.

have applied it in the testing of zinc-plated articles and used a 2 per cent solution of ammonium chloride as the corrosive medium, the immersions being made at 15-minute intervals. They concluded that this method of testing was much more discriminating for the materials used than the sodium chloride spray test and that the results checked well with observations of similar specimens in out-of-doors exposure. They stated that usually 120 hours of corrosion under these conditions developed rust on flat plates electroplated with a layer of zinc 0.0003

inch thick, whereas a few hours only was necessary to cause rust on similar plated articles of irregular shape.

In Figure 69 are summarized results obtained with steel coated in different ways when corroded with a solution of ammonium chloride by the intermittent immersion method [M 38].

Simple Immersion.

Tests of this character have not proved satisfactory as a rule as accelerated corrosion tests for zinc-coated materials. Wood has described [M 21] the results obtained for different types of zinc coatings when immersed in fresh water saturated with oxygen, up to 12 months' immersion. The results obtained enabled him to grade the various materials definitely on the basis of their resistance to corrosion under these conditions. The time required for some of the materials, particularly the hot-dipped and electroplated, was so long (12 months) as to render the method impracticable as a short-time test. For coatings such as nickel, however, which are cathodic toward iron, the simple immersion method is useful [M 25, *discuss.*] in revealing imperfections in the coating after a relatively short immersion. A small amount of an oxidizing agent such as hydrogen peroxide is sometimes added to a large volume of water, although water alone is generally used.

Exposure or Weathering Tests.

Without question, the final test of any material is that of service. The extensive field exposure tests of the various kinds of coated metal products now being conducted by the American Society for Testing Materials, through its Committee A-5, on the Corrosion of Iron and Steel [M 37], will in the course of time furnish information which is now lacking as to the service-life under fairly well-known atmospheric conditions of different types of zinc-coated products. The situations chosen for the exposure tests are representative of the atmospheric conditions prevailing in industrial cities, in the open country and along the seacoast, the latter in both temperate and subtropical climates. The weight of coating is in all cases to be determined as well as the behavior of representative samples toward the different accelerated-corrosion tests. It is only by such an impartial investigation that the real value of such tests can be definitely established.

Similarly the results of the exposure tests in the investigation of soil corrosion now in progress at the United States Bureau of Standards [M 36] may be expected to give some reliable information on the service life of zinc-coated materials when buried in soils of widely varying character. Such information is now almost entirely lacking.

Exposure tests of coated materials which have been subjected to bending or any other deforming process give very useful information. Such tests are properly to be considered as supplementary to the bend test rather than as simple tests of coating itself. They serve a very useful purpose, however, in showing how severe deformation, such as is encountered by sheet and wire in fabricating operations, these materials can be expected to withstand without any serious damage of the coating resulting.

One of the drawbacks in ordinary exposure tests of coated materials is the difficulty, and often the impossibility, of recording all the results and presenting them in a concise usable form for the benefit of those who have not seen the exposed specimens. Obviously only the essentials can be included in such a summary. In the case of zinc-coated materials these include the time necessary for the zinc layer to corrode sufficiently so as to expose first the underlying alloy layer of the coating and finally the base metal. Supplementary observations on the rate of corrosion of the base metal after the coating has been weathered away at any spot are also of value to show the degree of electrochemical protection given by the coating. With coatings used primarily for appearance, such as nickel or chromium, the time necessary for the appearance of rust and the extent of the rusting are the principal results to be revealed by an exposure test.

In the case of metals which, as a result of corrosion, undergo marked changes in some of their physical properties, the effectiveness of any protective coating can be much more accurately determined. For example, under certain conditions some of the aluminum alloys such as duralumin, especially in sheet form, may become seriously embrittled as a result of a corrosive attack. Tension tests of such material first in its initial state and then at intervals after exposure to the weather or some other corrosive condition will give very definite information as to the degree of protection afforded by any particular coating applied to the surface. In such tests the exposed samples are in the form of tension specimens, some in the uncoated state, others covered with the particular coating under investigation. Any serious breakdown of the coating whereby corrosion of the underlying metal results will be revealed by the changes which will be noted in the tensile properties of the material. Such a method, however, is not suitable for coated sheet iron or steel. The degree of corrosion necessary in order to affect the tensile properties of the metal to any pronounced extent would be so great and the visual evidence so unmistakable as to render a tension test unnecessary.

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O. CLEANING OF METAL SURFACES: PICKLING

The proper cleaning of metal surfaces is essential to success in any coating operation. The following references are given for convenience in looking up this subject. In Reference 1 are listed all the important articles on the subject up to 1924; equipment for pickling, pickling in acid solutions, pickling in salt solutions, electrolytic pickling, inhibitors and accelerators, effect of pickling on the properties of iron and steel and recovery of spent liquors.

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